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THE IODIDES OF NARCEINE.

BY G. B. FRANKFORTER.

Received April 16, 1894.

THE alkaloid narceine when treated with iodine forms a characteristic blue substance analogous in many respects to the blue substance formed by the action of iodine on starch. This blue substance was first observed by Stein[1] in the early history of the alkaloid who regarded it as a periodide of narceine; but as pure narceine was then unknown, and as no definite formula was given for the substance, due allowance must be made in accepting his work.

The isolation of pure narceine and the determination of the new empirical formula, as well as the synthetic structure,[2] has made it necessary to repeat all of the early investigations. So far, at present, as this repetition has been carried out, different conclusions have been reached. This fact explains in a degree the variations and contradictions of the early investigators. The formula of narceine was finally fixed by Anderson[3] as

$$C_{23}H_{29}NO_9,$$

and salts were prepared corresponding to

$$C_{23}H_{29}NO_9 . HCl \text{ and}$$
$$C_{23}H_{29}NO_9 . H_2SO_4.$$

Later work on the alkaloids shows that both the chloride and sulphates are not salts of the base

$$C_{23}H_{29}NO_9$$

but of a base containing one molecule of water less,

$$C_{23}H_{27}NO_8.$$

[1] *Fresenius' Zeitschrift für analytische Chemie*, 9, 390.

[2] Frankforter, "Beitrag zur Kenntniss des Narceïns." Inaug. Dis., Berlin.

[3] Anderson, *Liebig's Annalen d. Chemie. and Pharmacie.*, **86**, 182.

In like manner the iodides of narceine were found to be derivatives, not of the Anderson formula, but the same less one molecule of water.

The Blue Iodide. ($(C_{23}H_{27}NO_8)_3\,I_2 + 3H_2O$.) When narceine is treated with a water solution of iodine the blue iodide is formed, varying in color from a gray to an indigo blue, according to the amount of iodine used. By treating crystals of narceine direct with iodine, indigo-blue crystals are formed which still retain the same crystal form of narceine. By heating they change from long fine prismatic needles to short irregular ones. The blue crystals are slightly soluble in water, soluble with difficulty in alcohol, and quite insoluble in ether and chloroform.

On treating with dilute sodium hydroxide the blue color disappears, and when excess is avoided fine felt-like crystals of narceine are formed. By treating the blue crystals suspended in water with silver nitrate in the presence of nitric acid, beautiful hexagonal columns are formed which are now in process of analysis. The blue crystals contain three molecules of water which may be removed at 100° C.

0.3836 gram of the iodide lost 0.0118 gram at 100°.

Found, $3H_2O$.	Calculated for, $(C_{23}H_{27}NO_8)_3\,I_2 + 3H_2O$.
3.07 per cent.	3.29 per cent.

ANALYSES:

I. 0.2020 gram iodide gave 0.4050 gram CO_2, 0.1107 gram H_2O.
II. 0.2632 " " " 0.5294 " " 0.1424 " "
III. 0.3109 " " " 0.0912 " AgI.

	Found, I.	Found, II.	Found, III.	Calculated for, $(C_{23}H_{27}NO_8)_3\,I_2$.
C	54.65 per cent.	54.82 per cent.		54.63 per cent.
H	6.08 " "	6.00 " "		5.10 " "
I			15.95 per cent.	16.01 " "

Dried at 120°–130° the blue color changes to a brownish, but changes back to the blue on cooling. The dried substance melts at 176°–177° C. If heated rapidly a melting point of 180°–181° may be obtained.

The Red Iodide. $(C_{23}H_{27}NO_8)_3I$. It was found that by treating narceine with an alcoholic solution of iodine a grayish-blue substance was formed which proved to have different properties

from the blue iodide. On standing in the air, or by gently heating, it changes to a red color and loses its well-defined crystal form. Dried at 110°–120° it becomes brick red and changes slightly to the blue on standing some days in the air. It melts at 181° and is insoluble in water, alcohol, and ether. It contains three molecules of water which may be removed by drying at 90°–100°.

0.2209 gram iodide dried at 100°–110° lost 0.0092 H_2O.

Found, $3H_2O$.	Calculated for, $(C_{23}H_{27}NO_8)_2I+3H_2O$.
4.12 per cent.	3.56 per cent.

Analyses gave numbers which correspond best to the above formula.

ANALYSES:

I. 0.1826 gram iodide gave 0.3770 gram CO_2, 0.1025 gram H_2O.
II. 0.3763 " " " 0.0546 " AgI.

Found, I	Found, II	Calculated for, $(C_{23}H_{27}NO_8)_2I$.
C 56.35 per cent.		56.63 per cent.
H 6.23 " "		5.54 " "
I	7.84 per cent.	8.00 " "

Like the blue iodide it is transformed into narceine by carefully neutralizing with sodium hydroxide. In the presence of an alkali no iodide is formed. By treating with silver nitrate, slightly acidulated with nitric acid, fine long hexagonal columns crystallize out, on standing some hours in a cool place. The crystals are soluble in water and alcohol and melt at 110°–112°. They are in process of analysis. It will be observed that the analyses give the per cent. of hydrogen too high. This was also observed in a great many analyses made in determining the new formula for narceine. In all these analyses, some of which were made by professional analysts, the hydrogen ran too high. So that it is barely possible that the formula for narceine may be changed from $C_{23}H_{27}NO_8$ to $C_{23}H_{28}NO_8$. This would raise the per cent. of hydrogen to 6.24, while the average of ten analyses made by four analysts gave an average of 6.4 per cent. This work was begun in the University of Nebraska, and for many favors received there, I wish to thank Prof. H. H. Nicholson.

UNIVERSITY OF MINNESOTA.

SOME SOURCES OF ERROR IN OUR METHODS OF DETERMINING POTASH IN FERTILIZERS AND GERMAN POTASH SALTS.[1]

By N. Robinson, Reporter on Potash for the N. A. O. A. C. for 1893.

IN common with many others, the writer has for some time entertained the belief that none of our recognized or official methods for determining potash in fertilizers and potash salts were above criticism. The objections to our American official methods from German and other sources are entitled to the highest respect, and per contra, the grave doubts expressed in high quarters among chemists in this country, as to the validity of the superior claims made for the Anhalt or Stassfurt methods, determined the writer for his own satisfaction to undertake a series of experiments, to ascertain, if possible, the sources of error, if any should be found to exist, in the three best known and most widely used ways of potash determination; *viz.*, the official or Lindo-Gladding, the alternate, and the Stassfurt or Anhalt methods.

This series of experiments was begun over two years since, and has been prosecuted as time permitted from that period to the present. The writer is constrained to admit that he had at the beginning a very inadequate conception of the difficulties to be encountered in the solution of the problem, or the wide scope of inquiry which anything like an exhaustive study of the questions involved.

The literature of the matter, while sufficiently voluminous on the general subject of potash determination, seemed to stop short at the very point where these inquiries must begin. Teschemacher and Smith, with the sanction of Fresenius and the apparent acquiescence of all the best German authorities, had declared that the removal of sulphuric acid was a *sine qua non* in all accurate potash estimations which, of course, at once excluded our chief American method from the list of "accurate" ones. Then came Zimmerman with a general and certainly rather formidable indictment of this same method. He charged that the

[1] Read before the World's Congress of Chemists, August 22, 1893.

ammonium-chloride solution was far from being a harmless and indifferent solvent of the miscellaneous impurities which are usually found in the potassium-platinochloride precipitate as obtained by the Lindo-Gladding method. Exact details were, however, wanting, or, at least not obtainable in any publication within the reach of the writer. Since then it is understood that one or two chemists in this country have undertaken investigations similar to those made by the writer, albeit the results of their work, perhaps from his somewhat isolated position, have failed to reach him.

It is with no little hesitancy, and he trusts with becoming modesty, that he is compelled to come into court with a general indictment against all our recognized or official methods of determining potash in fertilizers and potash salts. The writer does not make this sweeping charge lightly or without a full estimate of its gravity and of the overwhelming weight of authority which is likely at once to be marshalled against it. Methods of recognized value and almost universal acceptance are not dislodged without a struggle. The writer can only plead the evidence of the facts which he gives, and look patiently to the "calm judgment of the coming time" for the vindication of views which are presumably too radical for general acceptance, except as the result of extended and patient research at the hands of abler investigators than himself.

The First Count Against All Three Methods.—The first count in the indictment, and which is common to all our methods, comes from an obscure phenomenon, which so far as I am aware, has never been thoroughly investigated. For want of a better name I shall call it "The occlusion of potash salts by precipitates." Certain precipitates have long been known to manifest this peculiarity; but the bearing of this upon potash estimation seems somehow to have been overlooked. The fundamental fact is this. Many precipitates carry down potash salts and hold them so tenaciously that they cannot be washed out with hot water. All the precipitates thrown down in the customary working of our various official methods manifest more or less of this same tendency. Barium sulphate is probably the worst offender. Ferric and aluminic compounds are scarcely less chargeable with

this occult species of chemical larceny, while calcium, magnesium, and the other salts of the alkali metals are by no means free from suspicion of at least a mild form of the same tendency to hide and hold potash.

The Lindo-Gladding Method.—According to the investigations of Zimmerman and others—investigations which the tabular estimates by the writer given below, seem to fully confirm, in addition to the above source of loss coming from the "occlusion" of potash in "precipitates," there are two other distinct and constant sources of error, with a number of casual and incidental ones, which may additionally vitiate results.

The first comes from the "alcohol washings" which, in the presence of the miscellaneous impurities nearly always found in the potassium platinochloride precipitate obtained by this method, result in the solution and consequent loss of the latter; and the second, from the fact that the solvent action of ammonium-chloride solution does not stop with the foreign salts which it is designed to remove; but that double decomposition often takes place. Potash is removed and ammonia substituted, involving the weighing of an impure potassium platinochloride, a portion of which is of different molecular weight. If we add to this the fact that calcium and magnesium sulphate, as well as ammonia, are not infrequently present in this same platinochloride, even when "washed to constant weight," we are certainly entitled to suspect the absolute correctness of all potash estimates made by the Lindo-Gladding method.

Before giving tabulated results the writer may be pardoned for outlining in the briefest manner, the methods used in the work. In all cases, precipitates were washed with hot water until some time after any cloudiness was perceptible in the filtrate, either with barium chloride or silver nitrate. Potash was recovered from precipitates thrown down by ammonia and ammonium oxalate by re-solution and reprecipitation, and from barium sulphate by boiling the filter and its contents twice in dilute hydrochloric acid. The recovery of the potash from the ammonium-chloride washings seems to present the greatest practical difficulty. The ordinary method of volatilizing the ammonium salts over an open Bunsen flame involved so much loss of potash that no reliance

could be placed on the results. Fair work was done by exposing the well-dried material in a thin layer, in a shallow flat-bottomed platinum capsule on a portion of the sand-bath where the heat could be kept at the lowest vaporizing temperature of ammonium chloride, and consuming five or six hours in the operation. Another method involving several evaporations, incinerations, and filtrations with a slight loss of potash, was to add to the washings enough sulphuric acid to change all bases into sulphates, with appropriate subsequent treatment. The recovery of the potash from the "alcohol washings" seemed to present no special difficulty.

A word as to the factor of correction used for the potash already present in the ammonium-chloride solution. In my first experiments I assumed that the amount of potash present could be correctly estimated "by difference," by simply subtracting the weight of the undissolved portion from the five grams of potassium platinochloride first placed in the 500 cc. of the washing-fluid. The factor, 0.000195 per cc. thus obtained was used until recently without a suspicion of its inaccuracy. Some inexplicably discordant results led to a careful review of the whole matter. Analytical determinations showed that nearly twice as much potash was present in my ammonium-chloride solution as I had supposed. On carefully carrying out the official directions with another lot of this ammonium-chloride solution, I found that the potassium platinochloride had done something else besides "settle over night." Mutual decomposition had taken place. The ammonium-chloride solution was found to contain about as much potash in the form of chloride as platinochloride. The undissolved portion was a mixture of potassium platinochloride and ammonium platinochloride. The final amount as ascertained by several analytical determinations of the solution actually used, was potash corresponding to 0.00039 potassium platinochloride to the cubic centimeter, and the work as now given is corrected by that factor.

Still another factor of correction, small in all probability but still necessary for exact work, may be casually referred to. It is more than doubtful whether the potassium platinochloride precipitate obtained by the Lindo-Gladding method—in spite of all

its numerous "washings"—is ever strictly chemically pure. My observations indicate that, in addition to ammonium platinochloride, calcium and magnesium sulphate, and sometimes other impurities, are almost certain to be present. In the limited time at my disposal, I was unable to devise any satisfactory plan for the estimation of these impurities, and the tabulated results are, therefore, given without this correction.

In regard to the last example given (No. 6), which was from the "mixed potash sample" sent out to chemists in this country and Europe, it may be said that the quantity taken, ¼ gram, is too small for accurate work, as every error is, of course, quadrupled in the final result. These estimates were the last made, and lack of material prevented the employment of a larger quantity. As the results tally fairly well, however, with the work of others, they are given for what they are worth.

It will be observed that the "alternate" method is to a certain extent liable to the same objection as the Lindo-Gladding. Most of the loss here comes from the "occlusion" of potash in the barium sulphate. How seriously this affects the final estimate may be seen from the tabulated results given below.

A large amount of work done in the same line of investigation is omitted, but all leading substantially to the same results.

The six examples given are, indeed, selected from some twenty that were more or less fully carried out. Those taken are those in which the amount of loss by washings and precipitates is the lowest. In the course of the work some very anomalous results were obtained. In one case as high as thirty-four milligrams of potassium platinochloride were recovered from a barium sulphate precipitate weighing only 320 milligrams, and from which boiling water had ceased to dissolve out any more potash. Faulty manipulation may in some way have affected the result; but I think that any chemist who attempts to wade through the mass of work that I have gone over, and to unravel the singularly tangled skein of surface or molecular forces which govern the behavior of potash salts in the presence of barium sulphate and other precipitates, will meet with a good many surprises. He will find first of all, that the accredited statement of most chemical authorities that potash salts are not carried down by barium sulphate in acid

solutions, is altogether a fallacy. He will find that the amount carried down is subject to wide variations, and that, too, under conditions seemingly identical. He will probably come at last to the conclusion that this whole subject of the occlusion of potash salts by precipitates needs thorough and exhaustive investigation; and that until it is done and the losses resulting therefrom are eliminated, we must write "doubtful" after every potash determination made by processes involving this very obscure but very positive source of error.

ANALYSIS OF MIXED FERTILIZERS CONTAINING BONE, BLOOD, ETC., TOGETHER WITH THE SAMPLE OF MIXED POTASH SALTS SENT OUT BY THE "REPORTER" BY THE LINDO-GLADDING METHOD WITH ESTIMATES OF LOSSES OF POTASH IN PRECIPITATES AND "WASHINGS." MADE AT THE FLORIDA STATE LABORATORY, NORMAN ROBINSON, ANALYST.

Mixed Fertilizer.	Amt. of material used in grams.	Weight of K_2PtCl_6 by Lindo-Gladding Method.	Weight of K_2PtCl_6 recovered from precip. by Am. and Am. Ox.	Weight of K_2PtCl_6 recovered from first alcohol washing.	Weight of K_2PtCl_6 recovered from washing with NH_4Cl solution with 2nd alcohol W.	Total weight of K_2PtCl_6 recovered from all sources.	Percentage of K_2O by Lindo-Gladding Method.	Percentage with losses added.	Percentage of loss.
1—With Bone, Etc.	½	0.3363	0.0030	0.0041	0.0051	0.0122	12.60	13.07	0.475
2—With Bone, Etc.	1	0.4040	0.0041	0.0034	0.0061	0.0136	7.80	8.06	0.26
3—With Bone, Etc.	1	0.2433	0.0031	0.0021	0.0033	0.0085	4.70	4.86	0.16
4—With Bone, Etc.	1	0.2114	0.0028	0.0031	0.0053	0.0112	4.10	4.32	0.22
5—With Phos. R'k.	½	0.3160	0.0084	0.0033	0.0018	0.0135	12.20	12.72	0.52
6—Mixed Potash Salts.	½	0.4884	0.0031	0.0042	0.0022	0.0095	37.70	38.43	0.73
Average loss to each 1 per cent. of potash estimated by Lindo-Gladding method.									0.029

ANALYSIS OF SAME BY THE "ALTERNATE" METHOD WITH SIMILAR ESTIMATES OF LOSSES IN PRECIPITATES AND WASHINGS.

	Amount taken in grams.	K_2PtCl_6 by alternate method.	K_2PtCl_6 recovered from Am. and Am. Ox. precipitate.	K_2PtCl_6 recovered from $BaSO_4$ precipitate.	K_2PtCl_6 from alcohol washings.	Total K_2PtCl_6 recovered.	Per cent. of K_2O by alternate method.	Per cent. with losses added.	Per cent of loss.
1—	½	0.3268	0.0021	0.0061	0.0024	0.0106	12.63	13.04	0.41
2—	1	0.3989	0.0015	0.0083	0.0036	0.0124	7.70	7.94	0.24
3—	1	0.2331	0.0024	0.0063	0.0024	0.0111	4.50	4.70	0.21
4—	1	0.2072	0.0010	0.0064	0.0033	0.0107	4.00	4.21	0.21
5—	½	0.3056	0.0022	0.0073	0.0031	0.0126	11.80	12.29	0.49
6—	½	0.4896	0.0015	0.0044	0.0038	0.0097	37.81	38.56	0.75
Average loss to each 1 per cent. of K_2O estimated by Alternate method.									0.29

The Stassfurt or Anhalt Method.—As our German friends are naturally very partial to the Stassfurt method of determining potash in potash salts, the writer was led to make some tests to determine whether the same or similar objections could be urged against it as are believed to lie against our American methods. Concerning this plan of estimating potash, it may be said that it is not likely to be popular until one acquires considerable facility in its use. The accurate precipitation of the sulphuric acid is pretty certain to give trouble at first. If, however, the precipitation be made in a vigorously boiling solution, this difficulty vanishes. The barium sulphate is then heavy and crystalline, and settles like so much sand. After considerable experience in its use the writer has come to prefer this German method to any other from the fact that it involves less manipulation, gives an unusually clean precipitate of potassium platinochloride, and generally requires less alcohol for washing. The writer is convinced, however that it is chargeable with the same essential defect as the Lindo-Gladding and the alternate methods. It does not estimate all the potash present. The barium sulphate manifests the same peculiarity here as elsewhere.

From a previous dissolved sample of the mixed German potash salts sent out by the reporter, 200 cc. was taken, corresponding to five grams of material, precipitated as accurately as possible with barium chloride and made after cooling to 251.25 cc., and after vigorous shaking set aside for a few hours to secure the complete subsidence of the barium sulphate. (The volume of the latter was determined at 1.25 cc. by calculation from the barium chloride used and confirmed by subsequent weighing.) Ten cc. accurately measured of the clear solution corresponding to one-fifth gram gave 0.392 of potassium platinochloride $\times 5 =$ 1.960 or 37.84 per cent., which closely approximate the average of the estimates made by German chemists; as much of the remaining liquid as could be moved without disturbing the precipitate was now poured off into a clean, dry beaker, and the precipitate with portions of this same solution was washed into an accurately calibrated fifty cc. measuring cylinder and again allowed to settle. After three hours the precipitate with the

mingled solution occupied a volume of sixteen cc. and did not seem inclined to go any lower. The clear liquid was now taken out with a pipette until exactly 21.25 cc. remained. The whole was now poured upon a dry nine cm. Schleicher and Schüll filter and exactly ten cc. filtered off and rejected. This of course left ten cc. of the solution and 1.25 cc. of the barium sulphate. The filter was repeatedly washed with hot water until no reaction was observable with silver nitrate. This last ten cc. of solution with the washings gave 0.4276 of potassium platinochloride or 22.6 mgms. more than the first ten cc. of solution examined, showing that this amount of potash was held up or occluded by the barium sulphate in a form that boiling water would remove. The filter with its precipitate was then boiled twice in twenty-five cc. dilute hydrochloric acid (one to five). In this way forty-four mgms. more potassium platinochloride were obtained. The total amount of potassium platinochloride recovered from the barium-sulphate precipitate was 66.6 mgms. or 0.01288 to each gram of substance = 0.247 per cent., or nearly one-fourth of one per cent. Other tests of the same material in smaller quantity gave considerably higher results, but as great care was taken to secure accuracy in every stage of the process, it is believed that the above fairly indicates the average loss where this particular material is estimated by the Stassfurt method. Much more extended investigations are required before any confident statements can be made as to the average loss from occluded potash when this method is employed.

Several other determinations exceeded this estimate. The instance given was carried out with special care. Full details of the methods used will be furnished to any one interested in the matter and perhaps not unfairly represents the average loss from this source.

In conclusion, it may be urged that, even conceding that there are some inherent defects in all our methods, since they are generally recognized and understood, and give fairly accurate results; anything looking towards a change is ill-timed and unwise. But what are we to consider "fairly accurate results?" As reporter on potash for the current year, the writer is compelled to echo an altogether too familiar refrain. We come up

here and, year after year, sing the same old tune. It is just as full of discord this year as it was last year and the year before that. To the question "How much potash?" working upon identically the same sample, New Hampshire says 12.13 per cent., New Jersey 12.76, New York and Maine 12.94, and North Carolina 13.08 per cent. and 13.22 per cent. Now here is a difference of considerably more than one per cent. in the same material, and that too, scattered along the whole gamut of rising estimates. Can these be considered "fairly accurate results?"

If we turn to our German friends, we find more unanimity but by no means complete agreement. Their answers to the same questions range from 13.10 per cent. to 13.44 per cent. Now who in this "confusion" of chemical tongues, has given us the right answer? Even on the face of it, is there not enough to suggest that there may be something wrong with the chemistry, as well as the chemists?

Notwithstanding the views and tabulated determinations above given, your reporter has no changes in existing methods to suggest. He only desires that the investigations he has outlined shall be submitted to careful re-examination, especially the "occlusion" of potash salts in precipitates, and that the relation of this as yet obscure phenomenon, to potash determination (a source of the error to which, so far as he is aware, the writer has now for the first time directed attention), should be made the subject of thorough investigation and review. If his conclusions are confirmed, changes are sure to come. Until then it seems the wiser course to adhere to existing methods.

[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF THE SCHOOL OF MINES, COLUMBIA COLLEGE.—No. 4.]

GANTTER'S PROCESS FOR DETERMINING THE IODINE FIGURE OF FATS.

BY PARKER C. MCILHINEY, PH.B., A.M.

Received March 31, 1894.

F. Gantter, (*Ztschr. anal. Chem.*, **32,** 178 and 181) proposes a new method of determining the iodine figure of fats and oils in which he uses carbon tetrachloride as a solvent for both the fat and iodine and uses no mercuric chloride as in the Hübl pro-

cess. He states that the figures obtained when mercuric chloride is used depend upon the amount used. The results which he obtained and from which he draws these conclusions are as follows:

Substance.	Amount iodine used.	Amount $HgCl_2$ used.	Iodine figure.
0.100 gram linseed-oil	0.100 gram.	0.050 gram.	83.5
" " " "	0.600 "	0.000 "	85.3
" " " "	0.150 "	0.250 "	141.0
" " " "	0.150 "	0.500 "	148.0
" " " "	0.600 "	0.250 "	156.4
" " " "	0.600 "	0.500 "	173.6
" " " "	0.600 "	1.000 "	188.4
" " lard	0.500 "	0.000 "	25.0
" " "	0.500 "	0.250 "	61.0
" " "	0.500 "	0.500 "	63.0
" " "	0.500 "	1.000 "	85.1

His results prove that the amount of mercuric chloride present influences the results and that a very large excess of Hübl's reagent would give a higher figure for linseed-oil than a moderate excess, but they certainly do not justify the conclusion which he draws from them that the use of mercuric chloride is unnecessary, and it is on this assumption that the accuracy of his process depends.

To ascertain whether fats would absorb from a solution of iodine alone in any suitable solvent as much iodine as would be necessary to convert them into saturated bodies, portions of a sample of oleic acid were treated with measured quantities of solutions of iodine in alcohol, carbon disulphide, and carbon tetrachloride. All these solvents dissolve both the oleic acid and iodine.

The results were as follows:

Solvent.	Amount of oleic acid.	Excess of iodine in cc. $\frac{N}{15}$ thio-sulphate.	Iodine figure.
Alcohol	0.9947 gram.	43.4	30.4
"	1.1445 grams.	43.5	26.1
Carbon disulphide ...	0.9791 gram.	58.9	52.7
" " ...	1.0044 grams.	59.0	51.3
Carbon tetrachloride.	0.1171 gram.	27.9	27.6
" "	0.1186 gram.	28.2	24.1

The iodine figure of the sample as determined by the Hübl process was 80.0.

These results show that iodine alone will not saturate fats and if it is used for this purpose its action must be assisted by mercuric chloride. Gantter's process, therefore, does not determine the iodine figure but an arbitrary figure which is not comparable with the results obtained by any other process.

THE CHEMICAL AND PHYSICAL EXAMINATION OF PORTLAND CEMENT.

(*Concluded from Page 372.*)

By Thomas B. Stillman, Ph.D.

REFERENCES (1870 to 1892).

1884.

Transactions of the American Society of Civil Engineers.—Method for ascertaining bulk of given weights, 13, 55. Cement first used in England, 13, 162. Hydraulicity: how conferred upon mortars by the ancients, 13, 162. Cement mixed with plaster Paris, 13, 64. Setting: curious failure and subsequent setting upon exposure to the air, 13, 65. Preliminary report of committee on a uniform system for testing cement, 13, 53, 63, 65. Testing machines, 13, 62.

Transactions of the American Institute of Mining Engineers.—Cement analyses, 180.

Zeitschrift für Analytische Chemie.—Untersuchungen über den Nachweis von Verfälschungen im Portland Cement, 175.

Jahresbericht (Wagner.)—Herstellung von Cement (L. Roth), 691; (W. Lesley), 691. Das basische Futter für Cementöfen von F. Morbitzer, 691. Cementbrennöfen von C. Dietszch, 691. Behandlung der Cemente mit Wasser (H. Lechatelier), 695. L. Tetmajer über: 1. Reinen Etagonofen Cement. 2. An der Luft zerfallenes Mehl aus dem Etagenofen. 3. Reinen Schachtofen-Cement. 4. An der Luft zerfallenes Mehl aus einem Schachtofen. 5. Portland Cement, gemahlen aus Schacht und Etagenofenklinkern, wie das in der Fabrik beim gleichzeitigem Betriebe vieler Ofensysteme üblich ist: 693. Ueber Gemische aus Kieselsäure und Calciumoxyd in Cemente (E. Landrin), 695. Bestimmung der Thonerde im Cement (H. Prunier), 697. Versuchsresultate über 194 verschiedene Cement proben (Böhme), 698. Prüfungsvorschriften für Cement ausgestellt von der Gesellschaft der amerikanischen Civilingenieure, 699. Tetmajer Rammeapparat, 701. Verfahren zur Prüfung von Portland Cement (W. Michaelis), 704. Ueber specifisches Gewicht Cementen (R. Fresenius), 707. Die Wirkung der Zumischmittel auf Portland Cement (Tetmajer, 711. Magnesia im Cement (L. Erdmenger), 712. Um Cement für stereochromatische Bemalung (V. Koch), 713.

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Engineering.—Slag as a basis of cement, **40**, 524. The testing of Portland cement (J. L. Spoor), **40**, 145.

Engineering News.—Portland cement—Porte de France **14**, 294. Mortars, **14**, 311, Adulterations (Fresenius), **13**, 365. Effect of sand on Portland cement, **14**, 22.

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Journal of the Society of Chemical Industry.—Analysis of cement, 247. Examination of Portland cement, 282. Gas kilns for cements, 90. Manufacture of Portland cement, 478, 542. Portland cement from slag, 179.

Proceedings of the Institution of Civil Engineers.—On the adulteration of Portland cement, **79**, 377. Natural and artificial Portland cements, **81**, 349. The action of certain admixtures on Portland cement, **81**, 349. The increased use of Portland cement, **80**, 17.

Scientific American Supplement.—Influence of sand on cement mortar, 7576. Uses of cement, 7787. Silicious cement, 8120.

Transactions of the American Society of Civil Engineers.—Behavior of cement mortars under various contingencies of use (Collingwood), **14**, 491. Coefficients of expansion by heat obtained by M. Bourriceau, 495. Fine grinding requisite for good cements, 377. Action of cement mixed with tallow and with clay, 164, 165. Specific gravity affected by fineness, 143.

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Zeitschrift für Analytische Chemie.—Ueber Portland cement und den Nachweis von fremden Zusätzer zu demselben, 66.

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Chemical News.—Influence of magnesia on Portland Cement **53**, 297.

Chemisches Central-Blatt.—Erhärtung des Cementes (Levoir), 541. Wesen der Hydraulizität (Michel), 748.

Comptes Rendus.—De l'influence de la Magnesie dans les ciments dits de Portland (G. Lechartier), 1223.

Dingler's Polytechnisches Journal.—Normen für einheitliche Lieferung und Prüfung von Portland Cement, **261**, 344. Untersuchung der sog. homogenisirten Schlackencementes (C. Schumann), 529. Ueber das Vermahlen von Schlackencement mittels Kugelmühlen, 530. Ueber die Leistung des Dietzsch'schen Cementbrennofens, 536. Ueber das Brennen des Cementes im Ringofen und Etagenöfen, 538. Ueber das Wesen der Hydraulicitat der Cemente, 538. Einfluss eines Zuckerzusatzes auf die Festigkeit von Cement-mörtel, **262**, 431.

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Engineering News.—The Böhme machine, **15**, 214. The Brendlinger machine, **15**, 310. Qualities of mortars and concretes, **15**, 82.

Journal of the Society of Chemical Industry.—Effect of adulterations on cement, 196. The hardening of cement, 492. Influence of magnesia, 492.

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Mittheilungen der Technische Laboratorium (München).—Verhandlungen der Münchener Conferenz und der von ihr gerwählten ständigen Commission zur Vereinbarung einheitlicher Prüfungsmethoden für Bau—und Construction-Materialen, 3, 143.

Proceedings of the Institution of Civil Engineers.—The rate of hardening of cement, **84**, 399, 411. Destructive action of cement mortar on lead piping, **84**, 472. Portland cement, **84**, 455. Blast-furnace slag compared with Portland cement, **85**, 415. Report of the U. S. Committee on Uniform System of Tests for Cements, **85**, 413.

Scientific American Supplement.—Sugar in cements, 9145. Magnesian cements, 9115. Uniform tests for cements, 8395.

Transactions of the American Society of Civil Engineers.—Alteration in dimensions, of Portland cement at various ages, **15**, 724, 726. Report of committee on the compressive strength of cements and settlement of masonry, 717. American natural cements, 877. Howe's Cave cement, 880. Rosendale cement, 877.

Jahresbericht (Wagner).—Arbeiten der Münchener Conferenz zur Vereinbarung einheitlicher Prüfungsweisen bei der Untersuchung von Cemente, 567–572. Definition von Portland Cement, 572. 1. Verpackung und Gewicht. 2. Bindezeit. 3. Volumbeständigkeit. 4. Feinheit der Mahlung. 5. Festigkeitsproben. Zür— und Druckgestigkeit, 572–576. Anfertigung der Cement-Sand-Proben, 576. Verwendung von Schlackencement (Tetmajer), 579. Wesen der Hydraulicität der Cemente (E. Michel), 585. Treiben des Portland Cementes (G. Lechartier), 587. Erhärten des Cementes (Levoir), 588. Nachhärtung von Portland Cementmörtel (F. Schiffner), 588. Herstellung von Portland Cement (W. Smith), 588.

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Chemical News.—Cement industry in Italy, **55**, 276.

Chemisches Central-Blatt.—Cementindustrie in Italien (Walter), 1096.

Dingler's Polytechnisches Journal.—Verhalten von Torf und Humus haltigem Sande bei der Mörtelbereitung, **263**, 342. Vallin's Gasofen mit Rührschaufeln zum Brennen von Cementpulver, **264**, 47. Heintzel's Herstellung eines Thonerdehydrat und lösliche Kieselsäure enthaltenden Zusatzmittels für Portland Cement, **247**. Ueber Hochöfenschlacke und Portland Cement, **265**, 184. Asphaltgründung, **264**, 45. Mischapparat, **265**, 593. Transportspirale, **264**, 628.

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Annales des Mines.—Recherches experimentales sur la couslution des mortiers hydrauliques (H. Le Chatelier), 345.

Journal of the Franklin Institute.—Improvements in Portland cement, **124**, 61.

Journal of the Society of Chemical Industry.—Influence of peaty sand on cements, 442. Influence of sugar, 140. Cement kilns, 767. Manu facture of cements, 292, 298.

Proceedings of the Institution of Civil Engineers.—Use of Portland cement in harbor works, **87**, 65. Cement-testing machines, **88**, 41. Prejudicial effect of magnesia in Portland cements, **87**, 161. Practical treatise on cement, **88**, 461. Testing of Portland cement for harbor works of Calais, **88**, 457. The effect of peaty impurites in Portland cement mortars, **88**, 463.

Scientific American Supplement.—Quick-setting cements, 9375. Manufacture of Portland cement, 9901.

Transactions of the American Society of Civil Engineers.—Absorption experiments on cements (Maclay), **17**, 215. Adhesion of cement to other materials (Faija), **17**, 220. Expansion and contraction of cements when hardening, **17**, 214. Strength of cements and settling of masonry, **17**, 213. Effect of salt water on the strength of cements, **16**, 80. Value of cements; how determined, **17**, 219. Briquette forms and molds for cement testing, **17**, 225. Compressive strength, **17**, 214, 216. Portland cement testing, **17**, 218. Effect of freezing, **16**, 79.

Mittheilungen der Technische Versuch Station (Berlin).—Resultate der Untersuchung von hydraulischem Kalk. Dr. Böhme **5**, 86, 95. Ueber die Abnutzbarkeit der Cemente und verschiedener Mörtel aus denselben Dr. Böhme, 108. Cement-Untersuchungen aus den Betriebsjahren, 1884, 1885, 1886. Dr. Böhme, **5**, 117.

Jahresbericht (Wagner).—Die Normen für die einheitliche Lieferung Prüfung von Portland Cement (Vereins deutscher Cementfabrikanten), 818–836. Begriffsbildung in der Mörteltechnik (E. Hartig), 839. Einheitliche Benennung der zur Mörtelbereitung gebrauchten Bindemittel (Tetmajer), 837. Einheitliche Bestimmung für die Lieferung und Prüfung hydraulischer Bindemittel (für die Schweiz), 840–845. Lufttreiben des Cementes (Tetmajer), 845. Ueber Luft und Wassermörtel (A. Schulatschenko), 848. Ueber Erhärtung der hydraulischen Mörtel (J. Foy), 849. Bestimmung des Adhäsionvermögens (E. Hartig), 849. Festigkeit der Cemente (R. Bose), 849. Herstellung eines Zusatzmittels für Portland Cement (C. Heintzel), 848. Die Cementindustrie in Italien (Walter), 849 Brennofen für Cemente, 850. Eine Siebmaschine für Cement (E. Kreiss), 853. Ueber die grosse Widerstandsfähigkeit des frischen Cementmörtels gegen Frost (A. Nobel), 853.

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Dingler's Polytechnisches Journal.—Grundmauerung, **267**, 478. Cementbeton zur Festungsbau, **267**, 475. Herstellung von Cement, **270**, 303. Spiritusbehälter aus Cement, **268**, 273. Ofen zum Brennen von Portland Cement, **270**, 292.

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Engineering.—The influence of sugar on cement, **45**, 102, 125. Painting upon cement, 297. The strength of cement, **45**, 80.

Engineering News.—Crushing strength of cements (Baker), **19**, 511. Economy in composition, **19**,.88, 177.

Journal of the Society of Chemical Industry.—Cement from lime mud, 301. Calcium salts in cements, 567. Cements, 325, 568, 631, 676.

Scientific American Supplement.—Bennert cement machine, 10300.

Transactions of the American Society of Civil Engineers.—Lime added to cement reduces strength, **18**, 268. Mixing machines, designed by E. L. Ransome, used in preparing cement for Sweetwater dam, **19**, 208. Percolation of water through cement mortar, **19**, 168. Compressive strength of cements, **18**, 264, 280. Cement-testing machines, **18**, 205.

Transactions of the American Institute of Mining Engineers.—Cement analyses 251. Cement rock in the black Hills, 571. In Ontario 294. Bituminous and hydraulic cements, 356.

Jahresbericht (Wagner). — Schachtofen zum Brennen von Cement (Thwaite, Collins), 818. Wirkung des magnesiahaltigen Cementes (Dyckerhoff), 818. Erhärtung von Portland Cement unter verschiedenen Bedingungen, 819. Herstellung der Druckprobekörper (Schumann), 822. Prüfung rasch bindender Cemente (Schiffner), 823. Das Verhalten des Cemente in Seewasser, 824. Brennöfen für Cement, 826. Brennen von Cement in Ringöfen (L. Erdmenger), 827. Sonnet's Cement Ofen, 827. Treiberscheinungen stark magnesiahaltiger Cemente (Böhme), 828. Raschbindener Cement (C. Heintzel), 828. Herstellung von Cement (J. Hargreaves), 828. Gemischte Portland Cement (W. Michaelis), 828.

Mittheilungen der Technische Versuch Station (Berlin).—Ueber Treiberscheinungen stark magnesiahaltiger Cemente, Dr. Böhme, **6**, 160.

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The Chemical News.—Practical study of Portland cement, **60**, 270.

Chemisches Central-Blatt.—Ueber Portland Cement, 168.

Dingler's Polytechnisches Journal.—Bindung der Kalkerde im Portland Cement, **271**, 138. Cement mit Zuckerzusatz zu seiner Erhärtung, **271**, 266. Prüfung von Cement, **271**, 471. Die Chemische Analyse, 471. Dichtigkeit, **271**, 472. Probenadel von Vicat, 472. Einfluss des Meerwassers auf die Bindezeit, 473. Versuche Candlot's über, Zugfestigkeit des Cementes, 474. Aenderung der Festigkeit mit der Zeit, 474. Einfluss der Temperature auf die Bindezeit, 474. Proben mit heissem Wasser, 475.

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Engineering News.—Slag cement, **22**, 531. Permeability of cements, **21**, 331. Austrian method of testing, **22**, 137.

Annales des Mines.—Note sur la fabrication des ciments (Prost), 158.

Journal of the Franklin Institute.—Permeability of Portland cement mortars, **127**, 219. Portland cement mortars, **128**, 199.

Journal of the Society of Chemical Industry.—Action of sea water upon cement, 48. Effect of sugar, 545. Influence of frost, 393. Portland cement, 543. Manufacture from alkali mud, 120, 462. Portland cement, 621, 622, 781, 782. Product of U. S., 590. Cements of the Isere, 887. Permeability of cements, 886.

Proceedings of the Institution of Civil Engineers.—Methods for testing Portland cements, **95**, 416. On the expansion of Portland cement, **96**, 357. Construction in cement on a metal skeleton, **97**, . The permeability of Portland cement and its decomposition by sea water, **97**, . The manufacture of slag cements, **98**, . Permeability of cement and cement mortars under pressure, **98**, 414. Manufacture of Portland cement of Isere, **98**, 415.

Scientific American Supplement.—Calcination of Portland cement, 11,398.

Transactions of the American Society of Civil Engineers.—Tamping: effect on strength of cement, **20**, 191. Cement used for Van Buren Bridge, **20**, 169.

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Mittheilungen der Technische Versuch-station (Berlin).—Ueber den Einfluss des Frostes auf die Festigkeit der Cemente. Dr. Böhme, **7**, 69. 1890.

Chemical News.—Repôrt on cement (Henry), **61**, 277.

Chemische Central-Blatt.—Cementuntersuchungen (Böhme), 952. Cementbildg (Sickenberger), 19. Konst. nach Kormanns Hydratisationstheorie (Zulkowsky), 175.

Dingler's Polytechnisches Journal.—Oefen zum Brennen von Portland Cement, **278**, 385. Schlackencement, **275**, 433.

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Engineering News.—Effect of salt water on cements, **24**, 544. Improvements in clips for testing machines, **24**, 544.

Journal of the Society of Chemical Industry.—Action of air and gases on cement, 73. Action of boiling water, 511. Composition for coloring Portland cement, 73. Rigley's direct process of calcination, 254. Errors in mixing with wet and dry sand, 1037. Hardening Portland cement, 72. Kilns for burning, 727. Magnesia in Portland cement, 943, 1037. Manufacture of Portland cement, 74, 512, 807, 522, 294, 1038, 863. Mills for grinding, 44. Portland cement from alkali waste, 509. Sulphate of lime in cement, 254.

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Scientific American Supplement.—Manufacture of Portland cement, 1204.

American Institute of Mining Engineers.—Cement from blast-furnace slag, 350.

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The Engineer.—Cement drying and burning apparatus, **71**, 53. The manufacture of cement, **71**, 85. Stokes Portland cement plant, 76, 126, 146, 164. A new era in cement testing, 391, 412. Michaelis Cement-testing machine, 493. Testing normal sand for cements, **72**, 195. Cement testing, 15.

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Engineering News.—Portland cement plant, **25**, 280. Microscopical tests (Brown), **26**, 481. Machine for briquettes, **25**, 138. Frost-proof, **26**,

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Journal of the Society of Chemical Industry.—Action of solution of magnesian sulphate on cement, 465. Apparatus for the manufacture of cement, 644. Proceedings of German cement makers, 390. Rapid method of testing soundness, 931. Wearing properties for paving purposes, 465. Comparative examination of Portland, Puzzolano, and Roman cements, 140. Hot tests for cements, 225.

Proceedings of the Institution of Civil Engineers.—Desirability of adopting a chemical test for Portland cement, **103**, 175. Slag cement, **105**, 427.

Scientific American Supplement.—Description of a new cement tester, 12526. Cement testing, 12838. Portland cement, 13308.

Transactions of the American Society of Civil Engineers.—Cement used as grout for filling voids in riprap under water, **24**, 230. Deterioration of cement by age, **25**, 269, 286. Neat test *vs.* sand tests for Portland cement, **25**, 295, 301, 303. Notes on cements, mortars, and concretes, **25**, 259. Seasoning of Portland cement, **25**, 282. Setting of Portland Cement, **25**, 279. Testing of cements (C. B. Brush), **25**, 270, 280. Tests of cements required by United States Navy Department, **25**, 261.

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ATTENTION IS ALSO DRAWN TO THE FOLLOWING WORKS PUBLISHED UPON CEMENT.

"Kalk, Gyps und Cement," by E. Böhmer und F. Newmann. Weimar, 1870.

"Patentirte Brennöfen—Anleitung zur Anlage der Zweckmässigsten Brennöfen für Thonwaaren, Kalk and Cement." Berlin, 1871.

"On limes, hydraulic cements, and mortars," by Gen. Q. A. Gillmore, U. S. A. New York, 1870.

"Notizblatt des deutschen Vereins für Fabrikation von Ziegeln, Thonwaaren, Kalk und Cement," by H. Seger. Berlin, 1873.

"Analyses chimiques et essais de resistance de matèriaux de construc-

tion, pierres de taille, chaux, ciments, plâtres, faits à l'ecole des ponts et chaussées sur la direction de MM. Léon Durand-Claye et Michelot, ingenieurs en chef des ponts et chaussées." Paris, Dunod, publisher.

"Die Bedeutung der Gasfeuerung und Gasöfen für das Brennen von Porcellan und Cement," von H. Stegmann. Berlin, 1877.

"Lehrbuch der Kalk, Cement und Gypsfabrikation," J. F. Rühne, Braunschweig. 1877.

"Jahrbuch über die Leistungen und Fortschritte der Thonwaaren, Kalk und Cement Industrie," von H. Zwick. Berlin, 1879.

"Hydraulischen Kalk, und Portland Cement nach Rohmaterialien, physikalischen und chemischen Eigenschaften, Untersuchung, Fabrikation und Werthstellung," von H. Zwich. Leipzig, 1879.

"On Portland cement," by James Forrest. London, 1880.

"Portland cement," by W. Maclay, C. E. New York, 1880.

"Science and art of the manufacture of Portland cement," by Henry Reed. London (Spon & Co.).

"Experiments on the strength of cement, chiefly in reference to the Portland cement used in Southern main drainage works," by John Grant; London.

"Calcaires, chaux, ciments, mortiers," par M. Duquesnay ingenieur des manufactures de l'etat. Paris, 1883 (Dunod, editeur).

"Traité Pratique de la Fabrication du Ciment de Portland," par A. Lipowitz. Paris, 1883 (Lacroix, editeur).

"A practical treatise on natural and artificial concrete, its varieties and constructive adaptations,," by Henry Reed. London (Spon & Co.).

"Résumés sur l'architecture et les sciences qui s'y rattachent," par A. Gouilly. Paris, (E. Bernard, editeur).

"Guide du chaufournier et du plâtrier, du fabricant de ciments, betons et mortiers hydrauliques." par Emile Lejeune. Paris, (Tignol, editeur).

"Maconnerie (chaux et ciments)," par J. Denfer, professeur à l'ecole centrale. Paris (Baudry, editeur).

"A text-book of the materials of construction," by R. H. Thurston. (Wiley & Sons) New York, 1885.

"Zement und Kalk, von Rudolf Tormin. Weimar, 1886.

"Kalk, Gyps, Cement," von Fr. Neumann. Weimar, 1886.

Étude pratique sur le ciment de Portland," par E. Candlot. Paris, 1886.

Die chemische Technologie der Mörtelmaterialien," von G. Feichtinger. Braunschweig, 1886.

"Ciments et chaux hydrauliques—fabrication, proprietes, emploi," par E. Candlot. Paris (Baudry, editeur), 1891.

"Der patentirte Sonnetsche Gas—Kanal-Ofen unter besonderer Berücksichtigung d. neuen Fabrikations Verfahren von Portland Cement." Bernburg, 1887.

"Die Fabrikation Stein, Cementgüsse," von E. Höfer. Vienna, 1887.

"Notes on Concrete," by John Newman. London (Spon & Co.).

"Chem. Grundbegriffe, Baumaterialienkunde Ziegel, Kalk-Gyps und Cementfabrikation," von Keller. Leipzig.

"Kalk, Gyps, Cementkalk und Portland Cement in Oestereich-Ungarn," von Carnawsky. Vienna.

"The testing of materials of construction," by W. C. Unwin, F. R. S. London, Eng., 1888.

Ètude sur la fabrication et les proprietes des ciments de l'Isèri," par M. A. Gobin, ingenieur en chef des ponts et chaussées. Paris, 1889. (Dunod, editeur).

"Protokoll der Verhandlungen des Vereins deutscher Cement-Fabrikanten." Berlin, 1890, 1891, 1892.

"Mineral resources of the United States," by David T. Day. Washington, D. C., 1891. "Natural and artificial cements," 527–529.

"Der Portland Cement und seine Anwendungen in Bauwesen: Bearbeiter im Auftrage des Vereins deutscher Portland Cement-Fabrikanten." Berlin, 1892.

"A manual of lime and cement," by A. H. Heath. London, 1893 (Spon & Co.

"Lehrbuch der Technische Chemie," von Dr. H. Ost. 1893, 179–190.

"Repertorium der Technischen Litteratur," von Bruno Kerl. Leipzig, 1870–1892.

"Chemisch-technische Analyse," von Dr. Jul. Post, 2, 16–29. Braunsweig, 1891.

"Chemisch-technische Untersuchungsmethoden," von Dr. F. Böckmann, 1, 683–727. Berlin, 1893.

"Thonindustrie-Zeitung," 1870–1892. Berlin.

"Chemische Technologie der Mörtelmaterialien," von Dr. Feichtinger, Braunschweig, 1885.

"Zeitschrift für Angewandte Chemie." 1889–1892.

"Chemiker-Zeitung, Repertorium." 1892.

"Mittheilungen des deutschen Veriens für Fabrication von Ziegeln, Thonwaaren, Kalk, und Cement." 1892.

"Deutsche Töpfer-u-Ziegler Zeitung." 1892.

"Deutsche Bauzeitung." 1892.

"A treatise on masonry construction," by Ira O. Baker. (Wiley & Sons) New York, 1893.

STEVENS INSTITUTE OF TECHNOLOGY, DECEMBER, 1893.

[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF THE SCHOOL OF MINES, COLUMBIA COLLEGE.—No. 5.]

THE QUANTITATIVE SEPARATION OF ROSIN OIL FROM MINERAL OILS.

BY PARKER C. MCILHINEY, PH.B., A.M.

Received March 31, 1894.

These two oils being both unsaponifiable are usually determined together as "unsaponifiable material" in the analysis of oils. They may be distinguished from one another by several methods.

1. *The Specific Gravity.*—Rosin oil has a much higher gravity than mineral oils, varying from 0.960 to 1.000 while heavy mineral oils range from 0.850 to 0.920.

2. *Valenta's Test.—Dingler's Poly. J.*, **252,** 297, and **253,** 418, *J. Chem. Soc.*, **48,** 93. Glacial acetic acid dissolves 2.67–6.50 per cent. by weight of mineral oil while rosin oil is soluble to the extent of 16.87 per cent. Mixtures, however, do not dissolve in proportion to the amount of rosin oil present.

3. *The Stannic Bromide Test.*—Allen, *Comm. Org. Anal.*, **2,** 463. A solution of stannic bromide in carbon disulphide gives, with small quantities of rosin oil in carbon disulphide solution, a purple coloration, while mineral oils do not.

4. *Solubility in Acetone.*—Demski and Morawski, *Dingler's Poly. J.*, **258,** 39. Acetone is miscible with rosin oil in all proportions while mineral oils require several volumes for solution.

5. *The Elaidin Test.*—Hager, *Ztschr. anal. Chem.*, **19,** 116. Rosin oil gives a dark red clear liquid while mineral oils remain unchanged.

6. *Ammonia Emulsion Test.*—Hager, *Muspratt's Tech. Chemie., 1893*, **4,** 127, mixes two cc. of the oil to be tested with two cc. of petroleum benzine and four cc. of water and after shaking adds one cc. of ten per cent. ammonia; he then shakes violently and allows to stand for one to two hours. A persistent milky layer indicates rosin oil.

7. *Action of Sulphuric Acid.*—Hager, *Ztschr. anal. Chem.*, agitates a portion of the oil with an equal volume of concentrated sulphuric acid for five minutes and then pours into several volumes of cold water. Mineral oil gives a white milky liquid which separates into two clear light-colored layers. Rosin oil gives a gray or brownish milky liquid which separates an upper layer of yellow-brown color full of opaque flocks.

8. *The Color Produced with Sulphuric and Acetic Acids.*—Storch, *Analyst*, **13,** 71. Two cc. of the oil is shaken up with one cc. of anhydrous acetic acid and warmed gently. After cooling, the acetic liquid is removed with a pipette and a drop of strong sulphuric acid added which immediately produces a brilliant red color if any rosin oil is present. Cholesterin in many fatty oils gives a similar reaction. The same author determines rosin oil

quantitatively by its solubility in alcohol which is greater than that of mineral oils.

9. *The Hübl Figure.*—Valenta, *Dingler's Poly. J.*, **253,** 420. The Hübl figure of rosin oil is forty-three to forty-eight, while that of mineral oils is below fifteen.

10. *The Refractive Index.*—Holde, *Mittheil d. chem. tech. Vers. Anst.*, *1890*, **8,** 269. With the Abbe refractometer the indices are as follows:

Rosin oil	1.5344
Mineral oils	1.4923

11. *Maumene's Test.—Muspratt Tech. Chem.*, *1893*, **4,** 128. Rosin oil gives a rise of temperature of 42° C. Mineral oils only a slight rise. Allen, *Comm. Org. Anal.*, **2,** 462, says the rise in temperature of rosin oil is 18°–20° C.

12. *The Action of Nitric Acid.—Muspratt*, **4,** 127. Nitric acid of 1.185 sp. gr. when heated with rosin oil reacts violently with it giving off copious red fumes while mineral oils are but slightly effected.

Allen, *Comm. Org. Anal.*, **2,** 462, says that cold nitric acid is sometimes without immediate action on rosin oil but on warming a violent reaction often very suddenly ensues and after cooling, the rosin oil is found to have been converted into a more or less brittle red resin.

This process was investigated with a view to making it quantitative. Attempts were made to use nitric acid of 1.42 sp. gr. at a boiling temperature, but the frothing of the mass proved a serious difficulty, the liquid in every instance frothing out of the flask. Acid of 1.2 sp. gr. was found more manageable, the frothing in this case being slight. It was thought that the red resin might be dissolved in alkali, in which it appears to be quite soluble, and leave behind the mineral oil which could be dissolved in benzine, but this process could not be made to work satisfactorily. It was found, however, that the red resin produced from the rosin oil was insoluble in petroleum ether while mineral oil dissolves easily.

The process was therefore altered by diluting the products of the reaction with water and extracting with petroleum ether.

The following process gave satisfactory results:

Fifty cc. of nitric acid of 1.2 sp. gr. are heated to boiling in a flask of 700 cc. capacity. The source of heat is removed and five grams of the oil to be analyzed added. The flask is then heated on the water-bath, with frequent shaking, for fifteen to twenty minutes, and about 400 cc. of cold water added. After the liquid has become entirely cold, fifty cc. of petroleum ether are added and the flask agitated. The oil which remains unacted upon dissolves in the ether, while the resin remains in suspension. The liquid is poured into a tapped separator, leaving the lumps of solid resin as far as possible behind in the flask. After settling, the aqueous liquid is drawn off and the ethereal layer poured into a tared flask. Another portion of petroleum ether is added to the resin remaining in the flask and allowed to act upon it for about ten minutes, when it is added to that in the tared flask. After distilling off the ether the oil is weighed. Mineral oils lose about ten per cent. in this way, and hence the weight of oil found must be divided by 0.9 in order to find the amount present in the sample analyzed.

Allen found mineral oils to lose ten to twelve per cent. on treatment with nitric acid. *Pharm. Jour.*, [3], **11**, 266.

A mixture of seventy-six per cent. of mineral oil with twenty-four per cent. of rosin oil gave, by this method, 76.8 per cent. of mineral oil.

RUTHENIUM AND ITS NITROSOCHLORIDES.[1]

By James Lewis Howe.

A FEW years ago A. Joly[2] published the results of an investigation on the supposed tetrachloride of ruthenium of Claus, in which he showed that the double salts of this compound, the "red salt" of Claus, are in reality double salts of a nitrosochloride, $RuCl_3NO$. When his work came to my notice I was engaged in studying the compounds of ruthenium, especially seeking to discover a simple and certain way of forming the supposed tetrachloride. Being engaged at present on other compounds of ruthenium, I present in this paper results reached,

[1] Read before the Cincinnati Section, March 15, 1894.

[2] *Compt. rend.*, **107**, 998; **108**, 854.

chiefly respecting the nitrosochlorides. For the unexpected formula of these compounds I am indebted to Joly, as at the time of his publication I had not analyzed any of the compounds; the rest of the work was entirely independent of his researches, and in the cases where the same work has been carried out by each of us, his results are in every respect confirmed.

The crude ruthenium was purified by fusion with caustic potash and saltpeter, and distillation of the dissolved melt in a stream of chlorine, as RuO_4. Good results were also obtained by treating the solution of the melt with potassium permanganate and sulphuric (or nitric) acid in the retort, and distilling. In either case the RuO_4 was received in dilute alcoholic potash. When the precipitate, or that obtained by treating a solution of the melt with nitric acid, is boiled for several days with aqua regia, in a flask provided with a return condenser, the ruthenium is completely converted into the nitrosochloride. (In his first paper Joly describes the formation of the nitrosochloride by treatment of $RuCl_3$ with a nitrite, and in his second paper by treatment with a large excess of nitric acid.) The solution in aqua regia is evaporated to dryness on a water-bath, the residue dissolved in water and treated with the chloride on an alkali; the corresponding double chloride then crystallizes out, either directly or on evaporation of the solution. The following salts have been studied, the analyses of the potassium and ammonium salts being given merely in confirmation of Joly's results.

1. *Potassium Ruthenium Nitrosochloride, or Potassium Nitrosochlorruthenate.* $2KCl, RuCl_3NO$, or K_2RuCl_5NO.—Formed by direct precipitation of very concentrated solutions of $RuCl_3NO$ with KCl solution, or by evaporation of the mixed solutions. The analyses, as well as those of the other salts, were made by heating the salt in a stream of hydrogen and collecting the hydrochloric acid evolved in a solution of silver nitrate. The nitrogen of the NO group is reduced and deposited in the cooler portion of the combustion tube as ammonium chloride. Claus' analytical error, which led him to the formula $2KCl, RuCl_4$, was in not directly estimating the evolved chlorine, the loss Cl_2NO differing very slightly in weight from Cl_4.

ANALYSIS.

	Calculated.	Found. I.	Found. II.
Cl_3NO (loss)	34.98	34.77	34.38
Cl_3	27.27	26.98	27.07
NO (difference)	7.71	7.79	7.30
Ru	26.77	26.65	25.99
2KCl	38.24	38.41	....
Cl_2 (in 2KCl)	18.18	....	18.62

SOLUBILITY.

At 25° ..... 100 parts water dissolve 12 parts salt.
At 60° ..... " " " " 80 " "

2. *Ammonium Ruthenium Nitrosochloride.* $2NH_4Cl, RuCl_3NO$. —Formed as above from $RuCl_3NO$ and NH_4Cl.

ANALYSIS.

	Calculated.	Found.
Cl_5	50.96	50.34
Ru	30.02	29.61

SOLUBILITY.

At 25° ..... 100 parts water dissolve 5 parts salt.
At 60° ..... " " " " 22 " "

3. *Rubidium Ruthenium Nitrosochloride.* 2RbCl, $RuCl_3NO$ and 2RbCl, $RuCl_3NO$, $2H_2O$.—When very concentrated solutions of $RuCl_3NO$ and RbCl are mixed there is precipitated a small amount of rather pale-purple anhydrous salt. If solutions less concentrated are mixed and evaporated over sulphuric acid, the hydrated salt crystallizes out in large crystals, accompanied by some of the anhydrous salt. On evaporating a solution of the hydrated salt to dryness on the water-bath, or even on heating its solution, it is almost completely converted into the anhydrous salt.

a. Anhydrous Salt.—Fine pale-purple powder, which may be recrystallized from hot water in small, almost black crystals, closely resembling the potassium and ammonium salts, and which, like these, give a pale-purple powder in the mortar.

ANALYSIS.

	Calculated.	Found. I.	Found. II.
Cl_3NO (loss)	28.27	.....	28.13
Cl_3	22.04	.....	21.89
NO (difference)	6.23	.....	6.24
Ru	21.64	.....	21.35
2RbCl (Rb = 85.2)	50.09	.....	50.52
Ratio Ru : 2RbCl	1 : 2.314	1 : 2.294	....
Ratio Ru : Cl_3	1 : 1.018	1 : 1.017	....

(I was a mixture of anhydrous and hydrated salt.)

SOLUBILITY.

At 25°..... 100 parts water dissolve 0.57 parts salt.
At 60°..... " " " " 2.13 " "

b. Hydrated Salt.—Large dark-purple crystals, losing their water of crystallization very readily over sulphuric acid, and difficult to completely free from the adhering anhydrous salt.

ANALYSIS.

	Calculated.		Found. I.		II.
Cl_3NO, $2H_2O$ (loss)	33.26		31.70		32.43
Cl_3	21.51		20.83		19.42
NO (difference).....	5.79	NO and $2H_2O$	10.87	NO	5.98
Ru	20.13		20.50		19.75
2RbCl	46.60		47.		....
$2H_2O$	6.96		....		7.03

(I had lost some water by standing over sulphuric acid before the first weighing was made.)

SOLUBILITY.

At 25°..... 100 parts water dissolve 114.3 parts salt.

4. *Cesium Ruthenium Nitrosochloride.* 2CsCl, $RuCl_3NO$ and 2CsCl, $RuCl_3NO$, $2H_2O$.—As with the rubidium salts, when very concentrated solutions of $RuCl_3NO$ and CsCl are mixed, cesium ruthenium nitrosochloride is partly precipitated as the anhydrous salt, while on evaporating the less concentrated cold mixed solutions over sulphuric acid, large crystals of the hydrated salt are formed. Some of the anhydrous salt is usually formed at the same time, even in the cold. On evaporating a solution of the very soluble hydrated salt on the water-bath to dryness, it is completely changed into the very slightly soluble anhydrous salt. I have not found it possible to form the hydrated salt from the anhydrous, nor to obtain the anhydrous salt in crystals large enough to be seen by the naked eye.

a. Anhydrous Salt.—Fine pale-purple powder, not differing in appearance from the rubidium salt, but less soluble.

ANALYSIS.

	Calculated.	Found. I.	II.	III.
Cl_3NO (loss)	23.61	23.85	....	23.56
Cl_3	18.41	17.93	18.19	18.41
NO (difference)	5.20	5.92	....	5.15
Ru	18.08	17.62	....	17.85
2CsCl (Cs = 132.7).....	58.31	58.40	....	57.90

SOLUBILITY.

At 25° ..... 100 parts water dissolve 0.20 parts salt.
At 60° ..... " " " " 0.56 " "

b. Hydrated Salt.—Large dark-purple crystals, often ten millimeters long or broad. Loses water of crystallization readily over sulphuric acid.

ANALYSIS.

	Calculated.	Found.
Cl_3NO, $2H_2O$ (loss)	28.10	28.11
Cl_3	17.32	16.92
NO (difference)	4.90	5.59
Ru	17.01	16.63
2CsCl	54.88	55.13
$2H_2O$	5.87	5.60

SOLUBILITY.

At 25° ..... 100 parts water dissolve 105.8 parts salt.

The properties of the nitrosochlorides agree almost, if not completely, with those ascribed to ruthenium tetrachloride by Claus[1] and M. C. Lea.[2] The most remarkable property, to which Joly has also called attention, is their stability.

Two and four-tenths grams of the potassium salt was heated with gradually increasing temperature in an air-bath. Up to above 250° the loss was less than 0.5 per cent. Direct heat was then applied to the crucible till the salt was partially decomposed, Cl and NO being evolved. The whole was then treated with water, and from the soluble portion the original undecomposed salt was crystallized. No trace of ruthenium trichloride was present, showing that the NO is not given off until the chlorine also passes off.

The solutions of the nitrosochlorides are unacted on by urea in acid or alkaline solutions, nor are they reduced by $FeSO_4$, Cu_2Cl_2, or $SnCl_2$. Hydrogen dioxide has no effect in acid solutions; in alkaline solutions oxygen is evolved, the solution becoming decolorized, but the change appears to be the same as that when the original solution is treated with excess of alkali.

Potassium permanganate has no reaction in acid solutions, but in alkaline solutions (with fixed alkalies) on boiling the green color of the manganate appears, soon followed by the

[1] *Bul. de l'Acad. Imp. de St. Pet.*, 1, 107; 4, 457.
[2] *Am. J. Sci.*, 38, 81, 248.

brown precipitate of the hydroxide, and the ruthenium salt is reduced to its trivalent condition. The solution after the reaction, gives the test for nitric acid, which is not the case with the original solution. It is then probable that the NO group is oxidized off by the permanganate.

Sodium hypobromite also reacts with the nitrosochloride in the cold, with evolution of gas; on acidifying with hydrochloric acid, RuO_4 is evolved with the bromine, a reaction analogous to the characteristic reaction of the trichloride with potassium chlorate and hydrochloric acid.

Potassium ferrocyanide gives no reaction in the cold with the nitrosochloride, but when *neutral* on boiling the solution becomes intensely deep brown, almost opaque unless very dilute. In acid solutions this reaction does not take place. Alkaline solutions become amber on boiling, but on careful neutralization with hydrochloric acid the brown coloration appears. An excess of acid changes the brown to a much less dense olive green, very different from the bright green produced by the trichloride with the ferrocyanide.

Sulphur dioxide has little effect in the cold, but when led into the warm alkaline solution of the nitrosochloride the solution gradually loses its rose color and becomes amber, and a precipitate is formed, very slightly soluble in water.

Potassium cyanide decolorizes the solution of the nitrosochloride on warming and a double salt seems gradually to be formed.

Oxalic acid has no apparent effect.

These last three reagents all have decided reactions with the trichloride and are now being further studied.

In the solutions of the heavy metals I have obtained no precipitates with the nitrosochloride, except with mercurous salts and those of silver. In both these cases a buff precipitate is thrown down, but on heating with nitric acid it is decomposed, the ruthenium passing into solution, the silver or mercurous chloride being left. Lead salts do not precipitate the nitrosochloride.

Copper sulphate gives no reaction, but on warming with excess of caustic alkali the copper hydroxide passes into solution, giving the azure-blue characteristic of Fehling's solution. From this, cuprous oxide is precipitated on warming with grape sugar.

When NO is led into a solution of ruthenium trichloride a change takes place, and the solution no longer gives the reactions for the trichloride; nor does it appear to contain the nitrosochloride. Differential characteristics for the nitrosochloride solutions as compared with the trichloride are the following:

Solutions rose becoming salmon pink on dilution.

No precipitate with excess of alkali.

No purple color on boiling with potassium thiocyanate.

No reaction with ammonia and sodium thiosulphate.

Deep brown on boiling with potassium ferrocyanide in neutral solution.

This last reaction is most characteristic.

Several attempts have been made by me to prepare a higher ruthenium chloride than the trichloride, but unsuccessfully.

RuO_4 dissolved in hydrochloric acid, yields on standing only $RuCl_3$; the same is true of RuO_4 dissolved in chlorine water.

RuS_2 was oxidized with HCl and $KClO_3$; much of the ruthenium was volatilized as RuO_4, while the residue consisted solely of $RuCl_3$.

In order to prove conclusively that the "red salt" of Claus was the nitrosochloride it was formed according to the method used by Claus; *viz.*, oxidation of RuS_2 with nitric acid.

ANALYSIS.

	Calculated.	Found.
Cl_3	26.77	26.95

It seems at first sight entirely unexpected that we should find the group NO directly connected with a metal, but it is by no means unique. The affinity of ferrous salts for NO is familiar, and there are several comparatively stable compounds in which the group NO appears to be attached to iron, as the nitrosopentasulphide and nitrosoheptasulphide, and the nitrosothiocarbonate. In the nitroprussides the NO group replaces in part the CN of the ferrocyanides. Iron and ruthenium occupy analogous positions in the periodic system, and as osmium is the third member of the series we should expect to find a similar and strong affinity of osmium for NO; indeed, Joly[1] has proposed to show that the osmiamic acid of Fritzsche and Struve has an

[1] *loc. cit.*

analogous constitution to the nitrosocompounds of ruthenium.

POLYTECHNIC SOCIETY, LOUISVILLE, KY.,
March, 1894.

ON THE CRYSTALLIZATION OF $2CsCl, RuCl_3NO, 2H_2O$ AND $2RbCl, RuCl_3NO, 2H_2O$.

BY N. D. CLARK.

These salts are isomorphous and crystallize in the monoclinic system. They show a similar habit and the crystals of both salts that were submitted for examination measured as much as ten millimeters in length.

The forms which were identified are

a, 100, $\bar{i}-\bar{1}$	*m*, 110, I	*e*, 101, $-1-\bar{1}$
c, 001, O	*d*, 021, $2-\bar{i}$	*o*, $\bar{1}01$, $1-\bar{1}$

The habit is prismatic like Figs. 1 and 2, while Fig. 3 represents a basal projection of Fig. 2. Of the forms in the prismatic zone *m* is always prominent while *a* is small and frequently fails. The prevailing forms that terminate the prisms are *d* and *o*, while *c* and *e* are usually either small or altogether wanting.

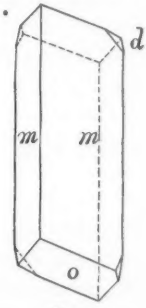


FIG. 1.

FIG. 2.

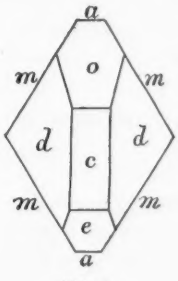


FIG. 3.

The axial ratios that are given beyond were calculated from the measurements that are marked by asterisks in the accompanying tables; the values cannot be regarded as very exact, as the crystal faces were slightly rounded and not adapted for accurate measurement. On the cesium salt the error in the fundamental measurements is regarded as not exceeding $\pm 8'$, while with the rubidium salt the error may exceed twice that amount.

$\dot{a} : \bar{b} : \dot{c}$

$2CsCl,RuCl_3NO,2H_2O$ 1.698 : 1 : 1.177 $\beta = 76°, 11'$

$2RbCl,RuCl_3NO,2H_2O$ 1.692 : 1 : 1.242 $\beta = 76°, 50\frac{1}{2}'$

		Measured.	Calculated.	Measured.	Calculated.
		$2CsCl,RuCl_3NO,2H_2O$.		$2RbCl,RuCl_3NO,2H_2O$.	
$a \wedge c$	100 ∧ 001	76°, 11′*	.....	76°, 50′, 30″*	.....
$c \wedge e$	001 ∧ 101	30°, 0′*	.....	31°, 18′	31°, 28′, 28″
$d \wedge d$	021 ∧ $0\bar{2}1$	132°, 45′*	.....	135°, 4′*	.....
$m \wedge m$	110 ∧ $\bar{1}10$	62°, 13′	62°, 27′, 59″	117°, 30′*	.....
$a \wedge m$	100 ∧ 110	58°, 45′	58°, 46′, 6″	58°, 50′	58°, 45′
$m \wedge d$	110 ∧ 021	33°, 18′, 30″	33°, 35′	.....	33°, 37′, 33″
$c \wedge o$	001 ∧ $\bar{1}01$	38°, 34′, 30″	38°, 53′, 23″	39°, 32′	40°, 37′, 9″
$a \wedge e$	100 ∧ 101	46°, 12′	46°, 11′	46°, 6′	45°, 22′, 2″
$d \wedge c$	021 ∧ 001	66°, 22′, 30″	66°, 30′	.....	67°, 32′
$a \wedge o$	$\bar{1}01$ ∧ 100	65°, 13′, 30″	64°, 55′, 37″	63°, 33′	62°, 32′, 21″

Both salts show a perfect cleavage parallel to *a* and a poorer one parallel to *c*. The plane of the optical axes is the clinopinacoid; the double refraction is strong, and the optical orientation such that cleavage plates parallel to *a* show in convergent polarized light an optical axis almost in the center of the field.

This investigation was made in the mineralogical-petrographical laboratory of the Sheffield Scientific School, under the direction of Prof. S. L. Penfield, to whom the author's thanks are due.

AN IMPROVED MERCURY THERMOMETER FOR HIGH TEMPERATURES.[1]

By W. Niehls.

THE ordinary mercury thermometers give accurate values up to 250° C. When the thermometer tube above the mercury is filled with nitrogen under pressure, readings are possible up to 450° C.

Early in 1893 I submitted to the Physikalisch-Technische Reichsanstalt, at Charlottenburg, Berlin, which, as is well known, tests the correctness of normal thermometers, etc., models of high temperature thermometers which were capable of giving accurate readings up to 550° C. Since then minor details of construction have been satisfactorily completed, and in the following, I will briefly describe the perfected instrument.

[1] Read before the Cincinnati Section, April 16, 1894.

At the outset it was necessary to secure a variety of glass which does not soften below 600°. For this purpose the borosilicate glass of Jena was chosen and has shown itself well adapted in all cases. The graduation is brought directly on the tube, and ranges either from 180° to 550° in single degrees, or from 100° to 550° in intervals of five degrees. The scale is black, for the sake of the greatest clearness, and the method of its preparation is as follows: The thermometer tube is supplied with the requisite amount of mercury, and then completely filled with carbon dioxide under a pressure of twenty atmospheres. In this condition the tube is heated and graduated. The mercury is then removed, black enamel is rubbed in the scale, and the tube is introduced into a muffle where the scale is brought out clearly in enamel.

This treatment in the muffle has not only the advantage of yielding a permanent scale which resists strong acids, but it also brings about an artificial "ageing" or "seasoning" of the thermometer. In other words, it decreases in a marked degree, the tendency of a thermometer to give too high readings as time goes on. This is evident from the following experimental data:

Thermometers graduated to 360°, which showed ordinarily a rise of 8°–10°, gave, after this preliminary treatment, when heated for ten hours to 340°–350° an increase of but 0.6°–0.8°. Those graduated to 400° showed, under the same conditions, a rise of 1.5°–2°. In the case of thermometers graduated to 550° the rise under the same conditions was 2°–3°. After further heating for ten hours the rise was 0.4°–0.6°. On the contrary, thermometers graduated to 550°, but not exposed to the "seasoning" treatment, showed, after being heated for ten hours, a rise of 16°–19°, and after a further period of ten hours a rise of 4°–6°, while further increase was naturally to be expected.

A further improvement of the high temperature thermometer is the coating on the back of the tube which greatly facilitates readings. This same result has been secured in the construction of ordinary thermometers by introducing into the back of the tube a strip of enamelled glass. The difference in the coefficients of expansion renders this impossible in the case of the high temperature thermometers. The strip of enamelled glass has been

replaced, however, very satisfactorily by a simple coating of enamel which is fused upon the surface of the tube at the same time that the figures of the scale are produced. The enamel on the rear of the tube, as well as that of the graduation, are totally unaffected after prolonged exposure to high temperatures.

An extended use of these thermometers is to be expected not only in laboratories, but in many branches of chemical industry, such as tar works, petroleum refineries, anilin works, etc.

I would mention in this connection the great help I have experienced in using Mahlke's "thread thermometer" for obtaining accurate readings at high temperatures. This gives the proper correction for the error due to the projection of a part of the mercury column of the thermometer outside of the substance or confined space, the temperature of which is being measured. In the case of long thermometers and high temperatures this error may reach 30°. Mahlke's thermometer is hung alongside the projecting part of a thermometer in use, and is so arranged as to give at once the reading for the number of degrees to be added to the temperature indicated in order to correct the error mentioned.

ON THE ESTIMATION OF SULPHUR IN PYRITES.[1]

By Thomas S. Gladding.

THERE are two recognized methods for the estimation of sulphur in pyrites which, with various modifications, are chiefly used by commercial chemists at the present time. These are:

First, the fusion of the ore with a mixture of sodium carbonate and potassium nitrate, solution in water, filtration from iron hydroxide, and precipitation as barium sulphate.

Second, the solution of the pyrites ore in aqua regia, or in aqua regia and bromine, and subsequent precipitation as barium sulphate.

The following investigation was undertaken to determine the relative merits of these two methods and the proper modifications to be observed:

A chemically pure potassium sulphate was examined for

[1] Read before the New York Section, March 9, 1894.

impurities with negative results. 2.7 grams containing about the amount of sulphur found in one gram of high grade pyrites were dissolved in 300 cc. to 400 cc. water, five cc. concentrated hydrochloric acid added, and a ten per cent. barium chloride solution added, at the rate of one drop per second, to the boiling solution. We obtained after standing over night:

Sulphur ..... 0.4960 gram.
" ..... 0.4960 "

Theory requires sulphur 0.4965. This amount of 0.496 gram was taken as the quantity of sulphur contained in 2.7 grams of the potassium sulphate, and the following series of experiments made exactly as above, with the stated additions and modifications. We first investigated the various conditions of the fusion methods.

Series I. With additions of five cc. nitric acid:

Sulphur found ..... 0.5007 gram.
" " ..... 0.5007 "
" " ..... 0.5020 "

The presence of nitric acid produces results too high, from the dragging down of nitrate salts, probably barium nitrate.

Series II. With addition of seventeen grams potassium nitrate:

Sulphur found ..... 0.5066 gram.
" " ..... 0.5102 "

Series III. With addition of fifteen grams of fusion mixture; *viz.*, sodium carbonate and potassium nitrate, and addition of hydrochloric acid to neutrality and five cc. in excess:

Sulphur found ..... 0.5005 gram.

Series IV. With addition of potassium chloride, 6.5 grams, sodium chloride, seven grams:

Sulphur found ..... 0.4955 gram.
" " ..... 0.4950 "
" " ..... 0.4966 "

No appreciable error either way.

The above series of experiments show that no *nitric* acid nor nitrates should be present in the solution at the time of precipitation. Series IV shows that when all nitric acid is expelled then sodium chloride and potassium chloride in solution will not cause error. We have found, however, that the complete expulsion of all nitric acid is a very difficult and tedious operation,

requiring repeated evaporations to dryness with excess of hydrochloric acid.

The practical difficulty of removing all the nitric acid, and time and labor required, are serious objections to this method.

The following experiments were made to investigate the conditions of the second or aqua regia method.

Series V. With addition of two grams of citric acid:

Sulphur found ..... 0.4960 gram.
" " ..... 0.4960 "

This shows that the citric acid, which is frequently used to keep up any iron present, does not exert a solvent action.

Series VI. With addition of two grams citric acid, and 0.500 gram iron, which is about the amount of iron in one gram of pyrites ore:

Sulphur found..... 0.4934 gram –0.4937 gram.
" " ..... 0.4937 " –0.4933 "
" " ..... 0.4940 " –0.4937 "
" " ..... 0.4938 " .....

This shows that the presence of iron causes low results.

The above results were obtained by ignition of the barium sulphate precipitate at low red heat until the filter paper was thoroughly burned. The precipitate was of a buff color.

On exposing the precipitates to a strong blast for several minutes longer they assumed a decided red color and lost weight.

The results were found to be:

Sulphur found ..... 0.4910 gram.
" " ..... 0.4913 "
" " ..... 0.4900 "

We attribute these erroneous results to the unavoidable dragging down of iron salts (probably iron sulphate) with the barium sulphate, and in place of an equivalent amount of barium sulphate. On ignition, this iron sulphate is decomposed, the sulphuric anhydride is expelled, causing low results, and the remaining iron oxide coloring the residue.

This was corroborated by taking 2.7 grams potassium sulphate, precipitating as above, drying the precipitate, brushing from the paper, drying at about 300° C., and adding the ash of the filter paper which had been burned in a separate dish.

Sulphur found ..... 0.4961 gram.

On heating over the blast-lamp for five minutes we found

Sulphur ..... 0.4880 gram.

It is evident that the presence of iron in the solution is incompatible with accurate results.

We next tried the method of Lunge and Hurter. They precipitate the iron with ammonia and throw down the barium sulphate in the filtrate.

Series VII. With addition of 0.5000 gram iron, precipitation of same with ammonia, and precipitation of barium sulphate in the filtrate:

Sulphur found ..... 0.4944 gram.
" " ..... 0.4935 "

These results were too low. On redissolving the ferric hydroxide (on filter paper) with hydrochloric acid, and adding barium chloride to the filtrate, and standing over night, we obtained a precipitate of barium sulphate, giving:

1. Sulphur ..... 0.0020 gram.
2. " ..... 0.0021 "

Adding these amounts we obtained:

Sulphur ..... 0.4964 gram.
" ..... 0.4956 "

The most careful washing failed to wash out all sulphur from the ferric hydroxide, and this solution in hydrochloric acid, and the separate recovery of sulphur contained therein, was found necessary.

These results were the most satisfactory yet obtained. The precipitate of barium sulphate was pure white, pulverulent and did not lose appreciable weight on prolonged heating over the blast-lamp. In this respect it differs from all precipitates hitherto obtained, demonstrates its far greater purity, and gives us a fixed and *final* result.

A method recently published instructs as follows: To the solution (about 200 cc.), heated on a steam-bath and containing twenty cc. free hydrochloric acid "add barium chloride solution from a burette, drop by drop, stirring briskly. Add thirty-five cc. and allow the solution to stand one hour on the steam-bath, filter through ten cm. paper and wash three times with hot water. Ignite and weigh barium sulphate." After calculating per cent.

sulphur, add 0.20 per cent. to the result for solubility of barium sulphate in the acidified liquid.

We tested this method using 2.70 grams potassium sulphate, 200 cc. water, twenty cc. hydrochloric acid, and 0.500 gram iron. We obtained:

Sulphur	0.4900	gram.
"	0.4898	"
"	0.4902	"
"	0.4894	"
"	0.4905	"

The average loss was found to be about 0.60 per cent. instead of 0.20 per cent. as stated. The color of the precipitate was light buff. On heating over the blast-lamp for five minutes the precipitate assumed a darker color and lost 0.021 gram in weight so that the percentage of sulphur was reduced about 0.30 per cent. more. Evidently this method does not produce a pure precipitate of barium sulphate.

The following series of comparative analyses on samples of pyrites received for assay, corroborates the above results. The results given under "Fusion Method" were obtained *without* evaporating to dryness to expel all nitric acid. The results given under "Bromine Method, No. 1," were obtained by solution in nitric acid and bromine, evaporation to dryness with hydrochloric acid, taking up with hot water, plus hydrochloric acid, addition of two grams citric acid and precipitation without removing the iron.

In "Bromine Method, No. 2," the iron was removed with ammonia and the barium sulphate precipitated in the filtrate. The ferric hydroxide was dissolved in dilute hydrochloric acid in a separate beaker, heated to boiling, barium chloride added, allowed to stand over night, and the small amount of barium sulphate thus obtained added to the main precipitate.

Samples.	Fusion method.	Bromine method, No. 1.	Bromine method, No. 2.
I	52.50	51.45	51.71
I	52.34	51.30	51.73
I	52.60	51.45	51.71
I	....	51.34	51.71
I	....	51.32	51.68
I	....	....	51.78

Samlpes.	Fusion method.	Bromine method, No. 1.	Bromine method, No. 2.
2	40.92	....	40.50
3	39.90	39.25	39.60
4	40.90	39.72	40.00
5	41.25	40.05	40.40
6	41.80	40.90	41.10
7	40.59	39.71	....
8	42.54	41.94	....
9	41.41	40.40	....

We see from the above that the "Fusion Method" without expulsion of all nitric acid gives results altogether too high, as was to have been expected.

The "Bromine Method," when iron is not removed, gives results too low by 0.20 per cent. to 0.35 per cent. This is in exact agreement with the previous work on pure potassium sulphate. No accurate allowance can be made on this method as the error will vary with the amount of heat applied in igniting the precipitate of barium sulphate.

In the "Bromine Method, No. 2," the precipitated iron hydroxide was redissolved in every case, and an additional amount of sulphur varying from 0.20 per cent. to 0.30 per cent. was obtained.

The insolubility of barium sulphate in the solution of ferric chloride thus obtained was demonstrated by dissolving 0.027 gram potassium sulphate in fifty cc. water, adding five cc. hydrochloric acid and 0.5 gram iron, precipitating hot and allowing to stand over night. We found:

1. Sulphur..... 0.0049 gram.
2. " ..... 0.0050 "
3. " ..... 0.0051 "

The amount actually present was 0.00496 gram.

As a result of the above investigation and of many comparative analyses of pyrites ores extending over several years, we have adopted the following method of assaying pyrites:

1. Grind the ore to an impalpable powder, dry at 100° C., and keep in well-corked bottles. Ten to fifteen minutes drying is sufficient.

2. Weigh one gram, introduce into beaker, cover with watch-glass, and add ten cc. bromine solution, mix by rotating beaker

and allow to stand ten minutes in the cold. Add ten cc. nitric acid, mix as before, and allow to stand ten minutes longer in the cold. Finally place the beaker on a water-bath, containing cold water, heat slowly to boiling, and when solution becomes quiet remove glass after rinsing and evaporate to dryness. Add ten cc. hydrochloric acid, keeping the beaker covered with a glass, and when violent action ceases, again remove the glass after rinsing, and evaporate to dryness once more. Add one cc. concentrated hydrochloric acid and fifty cc. hot water, digest until solution is complete, filter and wash with hot water. The filtrate, about 100 cc., is now saturated with a slight excess of ammonia, allow to stand hot for ten minutes. The precipitated ferric hydroxide is filtered and washed five or six times more on the paper with boiling hot water, the filtrate acidulated with hydrochloric acid in slight excess, heated to boiling and fifty cc. barium chloride solution added, one drop per second to the boiling liquid. The solution is allowed to stand over night, filtered, washed, and ignited, the precipitate of ferric hydroxide is also dissolved in dilute hot hydrochloric acid heated to boiling, and ten cc. barium chloride solution added. It is allowed to stand over night and the barium sulphate thus obtained added to the main precipitate. One filter paper can be used for the two precipitates.

The bromine solution is prepared by dissolving seventy-five grams potassium bromide in fifty cc. water, adding fifty cc. bromine, stirring and adding water to 500 cc. The bromine will nearly all dissolve. Another form of bromine solution used by some is made by saturating aqua regia with bromine. The first solution is the more certain, however, to oxidize all the ore without separation of any sulphur. The barium chloride is in ten per cent. solution.

Thanks are due to our assistants, Mr. H. E. Cutts and Mr. Thomas Brown, for valuable assistance in the analytical work of the above investigation.

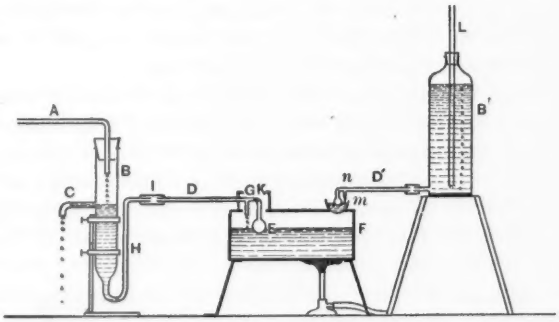
LABORATORY OF STILLWELL AND GLADDING,
NEW YORK.

A CONSTANT LEVEL APPARATUS.

By F. C. Robinson.

Received November 18, 1893.

THE following apparatus, which I have used for some time, may interest other chemists; hence the following sketch and description:



B is a glass tube about 2.5 cm. diameter into which is passed the small tube A through a cork. A side tube C extends out about ten cm. and is of much larger bore than A. Upon the lower end of B is sealed a small glass tube H which is bent up until opposite C, and then turned at right angles. Connected with H by a rubber tube is a tube D of equal bore and about twenty-five cm. long. Upon the other end of D is a bulb E, five cm. in diameter, turned down at right angles as shown in the cut. At the point G is a short tube and just beyond it at K, the tube D is closed up by melting it together. F is a water-bath through one of the openings of which E passes and floats upon the water. As the water rises in the bath, E, of course, floats higher, and raises the tube D. The rubber connector holds D upright and allows it to move. If B is clamped so that C and D are upon a level and the tap opened so that water flows into B through A, it will run out of both C and D, but of course D will soon float up so high that no water will run through it, and all will discharge at C. Now heat the bath and as soon as

evaporation has lowered D, sufficiently more water will run into the bath to take the place of that evaporated. A small stream of water flows constantly out at C and into the sink, but it need be very small indeed.

If the bulb E enters the bath through a place needed for evaporations, a small copper cylinder slightly larger than the opening and having a narrow strip cut out of it for D to move up and down in, may be placed over it as in the cut. Of course, the float may be placed in a side tube soldered to the bath with water-connection to it. If one cannot make it of glass it could easily be constructed of metal by any tinman.

I find also that the same idea works admirably for constant feeding of a small platinum dish in evaporating large quantities of water or other liquids for analysis of residues. In such cases the tube D′ is directly connected with a bottle holding several liters of water in the manner illustrated in the cut at the right. As D′ falls through evaporation of the water in *m*, air enters through L, and water drops out at *n* till D′ rises so that *n* is higher than the bottom of L, when it stops, and thus the level in *m* is constant. In this case the tube D′ is very small so that the bulb can be very small and still hold it up. In the one I use, the bulb is only 1.5 cm. in diameter and the tube *n* so close to it that it can be used in a crucible. It is very easy to clean the float from the slight residue clinging to it at the end.

I use the same apparatus for washing precipitates with a large amount of water, placing the bulb in the funnel on the surface of the wash-water.

BOWDOIN COLLEGE,
BRUNSWICK, MAINE, NOVEMBER 18, 1893.

A SCALE OF HARDNESS FOR GLASS.[1]

BY W. NIEHLS.

THE term "hardness" as applied to glass, refers to its degree of fusibility in the flame of the blast-lamp. Thus a glass which softens readily in the flame is called a "soft" glass, while one which softens with difficulty is called a "hard" glass. Between the extremes of a very soft and a very hard glass there

[1] Read before the Cincinnati Section, April 16, 1894.

is also quite a series of grades whose differences become very pronounced in actual glass working.

If this difference between two sorts be considerable it is impossible to effect permanent union by fusion between two samples. When the difference is slight, union may be effected between two sorts, but a condition of tension is produced which often causes later, a springing apart at the point of junction, even when not exposed to external strain. Permanent and satisfactory union is accomplished only when the varieties of glass are of the same, or nearly the same, hardness. Practiced glass-blowers make use of this fact in testing the sorts of glass placed at their disposal with reference to their power to unite. Samples of two sorts in the form of small rods are brought together evenly in a small pointed flame, heated therein uniformly, and when soft, fused together by pressure. They are then drawn slowly apart. The softer sample is drawn out more or less easily from the harder, so as to leave a quite pronounced edge when the difference in

Fig. 1.

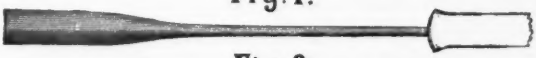


Fig. 2.

Fig. 3.

hardness is considerable (Fig. 1).

When differences are less marked or are even quite slight, the different lengths of the drawn-out ends are quite noticeable and the dividing line between the two sorts is evident to the eye (Fig. 2).

If the two sorts are of the same hardness both ends are drawn out evenly and there is no line of demarcation (Fig. 3).

Hitherto there has been no systematic classification of glass varieties according to hardness for the convenience of commerce, industry, and science. This lack I have supplied by the arrangement—with the co-operation of the German Physikalisch-

Technische Reichsanstalt—of a well-defined scale of hardness for glass, divided into eight degrees. The following are the typical sorts of glass for each degree:

I. The softest glass in commerce, French crystal.

II. Soft Thuringian glass, used for artificial flowers, toys, etc., English crystal.

III. Hard Thuringian glass, as used for thermometers, finer apparatus, etc.

IV. Jena normal thermometer glass (XVI''' of Schott and Co.).

V. French hard crystal used in Paris for normal thermometers (by Tonnelot).

VI. Jena boro-silicate thermometer glass (59''' of Schott and Co.).

VII. Jena thermometer glass free from alkalies (122''' of Schott and Co.). Both VI and VII are used for high temperature thermometers and many other purposes.

VIII. Cavalier's Bohemian crystal glass, used for combustion tubes, etc.

Normal scales of hardness for glass, arranged according to the above scheme, have been prepared and can be secured through dealers in chemical apparatus. They contain on cardboard, illustrative samples of the results of fusing (as described above), each number in the series with the next following number. Compartments also are well stocked with small rods of each degree on the scale—each rod stamped with its number—to be used for testing.

The use of such a scale brings a most desirable element of certainty into the glass trade as well as into the technique of physical and chemical laboratories, and many industrial operations.

[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF THE SCHOOL OF MINES, COLUMBIA COLLEGE.—NO. 6.]

A METHOD OF DETERMINING THE KOETTSTORFER FIGURE OF DARK-COLORED SUBSTANCES.

BY PARKER C. MCILHINEY, PH.B., A.M.

Received May 5, 1894.

THE Koettstorfer figure of a fat or resin is the number of milligrams of potassium hydroxide required to saponify one gram of the substance. It is determined by adding to a

weighed quantity of the substance a measured excess of an alcoholic solution of potash, evaporating off the alcohol, redissolving in neutral alcohol, and determining the excess of potash by standard hydrochloric acid. When the substance is light in color and the alcohol free from aldehyde, the determination is easily made, but if the substance has much color of its own the end reaction with phenolphthalein is indistinct. The same is true if the alcohol used contains aldehyde, as this gives with caustic potash a red-brown color. The latter difficulty can be surmounted by purifying the alcohol, but the former one is more serious. In experimenting to find a mode of procedure which would obviate the difficulty it was observed that a solution of neutral soap, to which ammonium chloride had been added, when submitted to distillation liberated a quantity of ammonia equivalent to the alkali combined with the soap.

Based on this principle the following method was devised: Two grams of the substance under examination is weighed into an Erlenmeyer flask, an excess of an alcoholic solution of caustic soda added, and the alcohol evaporated off. 250 cc. of ninety-three per cent. alcohol is now added and the solution heated until the soap is dissolved. Carbonic acid gas is now passed through the solution for about one hour. This treatment converts the free caustic alkali present into carbonate and bicarbonate which precipitate. The solution is then filtered into a suitable flask and most of the alcohol distilled off. It is necessary to add a spiral of platinum wire or a piece of sharp pointed metal or glass to prevent boiling over. When most of the alcohol is gone a solution of ten grams of ammonium chloride, in 100 cc. of water, is added and the solution distilled as far as possible, the distillate being caught in twenty cc. of normal hydrochloric acid which is titrated at the end of the operation, using methyl orange as indicator. The amount of hydrochloric acid neutralized by ammonia is equivalent to the combined alkali in the test.

Alcohol of ninety-three per cent. was found to dissolve sodium bicarbonate sufficient to neutralize 0.34 cc. of normal acid for every 100 cc. of alcohol used. A deduction must therefore be made for this in the calculation.

A sample of linseed-oil tested in this way gave a Koettstorfer

figure of 192.4, and by the ordinary process the figure found was 193.1. A sample of dragon's blood resin gave 124.9.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI. XLV.]

ON THE VOLATILITY OF BORAX.[1]

BY SIGMUND WALDBOTT, PH.D.

THE fact that borax is a volatile substance under ordinary laboratory conditions seems to have, hitherto, escaped notice. No reference is made to it in the literature of pure chemistry, and the following quotation from E. Cramer[2] would imply a general belief among technical chemists to the contrary:

"The boric acid must not be added in the form of vitreous boric acid, but in the form of sodium borate, whereby no volatilization will take place."

In the course of an investigation on the borates, carried on in connection with Prof. T. H. Norton, certain observations led to the suspicion that borax was not entirely unaffected by the heat of the ordinary blast-lamp.

A series of quantitative experiments was made, the results of which may be briefly summarized as follows:

If a small amount of pure borax, say four grams, be heated in a platinum crucible of fifty cc. contents, until the water of crystallization is quantitatively given off, and if the residue, borax glass, then be heated over a Bunsen burner for about ten minutes or longer, the weight will be found constant. If the crucible, half covered by the lid, be next heated over a gentle blast-flame, there will be noticed a very slight, yet distinctly perceptible loss in weight, increasing in proportion to the intensity of heat and the time of heating.

If now the uncovered crucible with its contents be subjected to an intense white heat, heavy vapors arise from the surface of the molten borax glass, and if heating is prolonged a very marked decrease in weight becomes evident.

The following experimental results are classified according to the general temperature maintained:

[1] Read before the Cincinnati Section, February 15, 1894.

[2] E. Cramer, *Thonindustrie-Zeitung*, *1892*, p. 155.

A. Volatility at Higher Temperatures.

The experiments recorded under this heading were all carried out at a white heat, as high a temperature as could be obtained by the ordinary laboratory blast-lamp. The borax used in these experiments, unless expressly stated otherwise, was purified by recrystallization and by drying for about twelve hours on unglazed porcelain.

I.

1.2500 grams $Na_2B_4O_7+10H_2O$, when heated, lost 0.5968 gram H_2O=47.74 per cent. (Theoretical loss=47.12 per cent., drying on unglazed porcelain was omitted.)

0.6532 gram borax glass remained and was heated as follows:

Time of heating, minutes.	Mode of heating.	Loss each time, gram.	Total loss, gram.	Total loss in per cent.
5	Crucible uncovered	0.0055	0.0055	0.8
7	" covered	0.0010	0.0065	1.0
10	" uncovered	0.0060	0.0125	2.0
7	" half covered, chimney used	0.0039	0.0164	2.5
10	" uncovered	0.0054	0.0218	3.3
5	" "	0.0050	0.0268	4.1
2	" "	0.0009	0.0277	4.2

0.6532 gram borax glass lost 4.2 per cent. in forty-six minutes.

II.

7.9201 grams $Na_2B_4O_7+10H_2O$, when heated, lost 3.7356 grams H_2O=47.17 per cent. (Theoretical loss=47.12 per cent.)

4.1845 grams borax glass remained and were heated as follows:

Time of heating, minutes.	Mode of heating.	Loss each time, gram.	Total loss, gram.	Total loss in per cent.
5	Crucible open	0.0085	0.0085	0.23
10	" half covered	0.0040	0.0125	0.298
10	" " " chimney used	0.0045	0.0170	0.406
	Lid, covered with drops, was heated	0.0023	0.0193	0.461
10	Crucible open	0.0080	0.0273	0.652
10	" "	0.0076	0.0349	0.834

4.1845 grams borax glass lost 0.83 per cent. in forty-five minutes.

In comparing the results of these two experiments it will be seen that the absolute amount of borax evaporated in a given time is about the same in both cases, whether a large or a small quantity is used, indicating that the amount volatilized at a given high temperature depends chiefly on the surface of the fused mass.

In the following three experiments it was sought to determine in what form borax is volatile.

It is possible that either borax is volatile as such, or that it is dissociated at high temperatures, giving off B_2O_3 and leaving Na_2O behind. An analysis of the residue after heating borax glass for a certain length of time would decide; for in case B_2O_3 is evolved the percentage of Na_2O must be higher than if borax as such is volatilized. As the difference between the two values for Na_2O under the latter supposition would increase rapidly with the loss in weight, samples of borax glass were heated long enough to bring about a loss of some twelve per cent.

III.

1.5630 grams $Na_2B_4O_7+10H_2O$, lost on heating 0.7380 gram H_2O=47.21 per cent. (Theoretical loss=47.12 per cent.)

0.8250 gram borax glass remained and was heated as follows:

Time of heating, minutes.	Mode of heating.	Loss each time, gram.	Total loss, gram.	Total loss in per cent.
20	Crucible partly covered	0.0106	0.0106	1.3
20	Crucible covered, small space allowed, fine drops on lid	0.0020	0.0126	1.6
	The lid alone was heated	0.0060	0.0186	2.3
20	Crucible uncovered	0.0171	0.0357	4.4
60	Crucible uncovered	0.0365	0.0722	8.8
60	Crucible uncovered, heat less intense	0.0210	0.0932	11.34

0.8250 gram borax glass lost 11.34 per cent. in three hours.

The residue weighed 0.7318 gram, and was analyzed, yielding 0.2185 gram Na_2O or 29.85 per cent.

	Theory, if loss were B_2O_3.	Theory, if loss were $Na_2B_4O_7$.	Found.
Na_2O	34.62 per cent.	30.69 per cent.	29.85 per cent.

IV.

1.5691 grams $Na_2B_4O_7+10H_2O$, lost on heating 0.7387 gram H_2O=47.07 per cent. (Theoretical loss=47.12 per cent.)

0.8304 gram borax glass remained and was heated as follows:

Time of heating, minutes.	Mode of heating.	Loss each time, gram.	Total loss, gram.	Total loss in per cent.
30	Crucible open	0.0134	0.0134	1.6
90	" "	0.0565	0.0699	8.4
35	" "	0.0220	0.0919	11.07
20	" "	0.0121	0.1040	12.52

0.8304 gram borax glass lost 12.52 per cent. in about three hours.

The residue weighed 0.7264 gram, and yielded on analysis 0.21796 gram Na_2O.

	Theory, if loss were B_2O_3.	Theory, if loss were $Na_2B_4O_7$.	Found.
Na_2O.....	35.09 per cent.	30.69 per cent.	30.01 per cent.

The low results obtained for Na_2O in III and IV were found to be due to a slight loss liable to be incurred in the analytical process used (treatment with ammonium fluoride), which will be touched upon in a communication following this. This source of error was obviated in the following experiment:

V.

0.9350 gram borax glass was heated as follows:

Time of heating, minutes.	Mode of heating.	Loss each time, gram.	Total loss, gram.	Total loss in per cent.
60	Crucible uncovered.....	0.0387	0.0387	4.1
120	" "	0.0914	0.1301	13.91

0.9350 gram borax glass lost 13.91 per cent. in three hours.

The residue weighed 0.8049 gram, and yielded on analysis 0.2439 gram Na_2O.

	Theory, if loss were B_2O_3.	Theory, if loss were $Na_2B_4O_7$.	Found.
Na_2O.....	35.65 per cent.	30.69 per cent.	30.31 per cent.

These results show beyond doubt that borax is volatile as such, and are corroborated by the following observations:

A thin film of borax glass on the inside of a crucible can be entirely volatilized by persistent heating.

The drops which occasionally gather on the lid of the crucible in the experiments described, can also be driven off completely by continued heating.

SUMMARY OF THE RESULTS OF EXPERIMENTS A, I–V.

Losses in per cent. at the end of	Weights of Borax Glass. I, 0.6532 gram.	II, 4.1845 grams.	III, 0.8250 gram.	IV, 0.8304 gram.	V, 0.9350 gram.
5 minutes.....	0.8	0.23	...	...	...
12 "	1.0	....	...	...	...
15 "	...	0.298	...	...	...
20 "	...	....	1.3	...	...
22 "	2.0	....	...	...	...
25 "	...	0.461	...	...	...
29 "	2.5	....	...	...	...
30 "	...	....	...	1.6	...
35 "	...	0.652	...	...	...

Losses in per cent at the end of		Weights of Borax Glass. I, 0.6532 gram.	II, 4.1845 grams.	III, 0.8250 gram.	IV, 0.8304 gram.	V, 0.9350 gram.
39	"	3.3	....	...	...	...
40	"	...	....	2.3	...	...
44	"	4.1	....	...	...	...
45	"	...	0.834	...	...	...
46	"	4.2	....	...	...	...
60	"	...	....	4.4	...	4.1
120	"	...	....	8.8	8.4	...
155	"	...	....	...	11.07	...
175	"	...	....	...	12.52	...
180	"	...	....	11.34	...	13.91

These values obtained for the volatility of borax at high temperatures suggested the study of the behavior of borax glass at a lower heat, with the following results:

B. Volatility at Lower Temperatures.

I.

4.0199 grams $Na_2B_4O_7+10H_2O$ were heated in a platinum crucible until the water was expelled and the weight was constant.

Water expelled=1.887 grams=46.96 per cent. (Theoretical loss=47.12 per cent.

2.1320 grams borax glass remained and were further heated as follows:

Time of heating, minutes.	Mode of heating.	Loss each time. gram.	Total loss, gram.	Total loss in per cent.
10	Bunsen burner with chimney, full flame	0.0000	0.0000	0.000
15	Moderate blast-flame, crucible half covered	0.0014	0.0014	0.065
15	Moderate blast-flame, crucible half covered, drops noticed on lid	0.0008	0.0024	0.112
20	Moderate blast-flame, crucible half covered, drops noticed on lid	0.0020	0.0044	0.206
5	Strong blast-flame, crucible open	0.0048	0.0092	0.431
10	" " " " "	0.0073	0.0165	0.774
60	Bunsen burner, full flame, crucible half covered	0.0000	0.0165	0.774

II.

2.4425 grams borax glass were heated for ten minutes over a strong blast-flame in order to insure perfect expulsion of water.

It weighed then 2.4327 grams and was further heated as follows:

Time of heating, minutes.	Mode of heating.	Loss each time, gram.	Total loss, gram.	Total loss in per cent.
30	Bunsen burner, strong flame, crucible half covered	0.0000	0.0000	0.000
15	Gentle blast-flame, crucible half covered	0.0015	0.0015	0.061
15	Gentle blast-flame, crucible half covered	0.0017	0.0032	0.131

III.

0.6148 gram borax glass after being heated for a short time over a strong blast-flame, weighed 0.6126 gram and was further heated as follows:

Time of heating, minutes.	Mode of heating.	Loss each time, gram.	Total loss, gram.	Total loss in per cent.
15	Stronger blast-flame, crucible half covered	0.0034	0.0034	0.555
15	Gentle blast-flame, crucible half covered	0.0016	0.0050	0.816
15	Gentle blast-flame, crucible half covered	0.0018	0.0068	1.110

SUMMARY OF THE RESULTS OF EXPERIMENTS B, I–III.

Weight of borax glass.	Loss in per cent. at the end of 15 minutes, per cent.	30 minutes, per cent.	45 minutes, per cent.	50 minutes, per cent.
2.1320 grams	0.065	0.112	....	0.206
2.4327 "	0.061	0.131	....	....
0.6126 gram	0.555	0.816	1.110	....

The question here suggests itself how this behavior of borax might influence the accuracy of such determinations of boric acid as involve exposure of a borate to high temperatures, as for example in the determinations of boric acid by the methods of H. Rose and G. Schaffgotsch. (v. Fresenius Quant. Anal.)

As in these determinations borates of a higher basicity than borax are formed, the results just given, cannot be with certainty utilized, although the more basic borates are probably less volatile than borax. But even supposing these more basic borates to be as volatile as borax itself, a material error from this source can occur only, if there be but a small amount of the borate subjected to analysis, and if the expulsion of carbon dioxide be attempted at too high a temperature and maintained for an unduly long time.

To illustrate such an exceptional case let us refer for instance to the experiment under A I, where it is shown that 0.6532 gram borax glass lost in weight 0.0125 gram=two per cent., when exposed to a white heat for twenty-two minutes, while the crucible was uncovered for fifteen minutes.

If, therefore, 0.2805 gram boron trioxide be analyzed by the method of G. Schaffgotsch this amount would be equivalent to 0.6532 gram of the borate $B_4O_9Na_6$ formed in this process; this salt would lose in weight two per cent. in twenty-two minutes, if exposed to a white heat, if we assume that it be exactly as volatile as borax under the same conditions.

There would then remain 0.6401 gram of the borate, containing 0.2749 gram of B_2O_3, which implies a loss of B_2O_3 equal to 0.0056 gram or 1.99 per cent.

It is, however, evident from the above that a loss from volatilization of the borate will fall within the errors of manipulation, when in an analysis a normal amount of boric acid is taken, say not less than one gram and when the heating is maintained for about ten minutes at not too high a temperature. This is under the assumption that borates of a higher basicity than borax are volatile to the same extent as the latter. Whether this is the case or not I have not attempted to ascertain, but a preliminary experiment made with a borate of approximately the composition $B_4O_9Na_6$ shows that an increase of basicity in the molecule of borax does not guard the more basic borate from volatilization entirely, for I observed with this borate the same phenomena noticeable when heating borax; *viz.*, the evolution of heavy vapors from its surface, implying a loss in weight when subjected to a white heat. A statement contrary to this fact was made by G. Schaffgotsch[1] in claiming that the salt formed by the action of one and a half molecules of Na_2CO_3 on one molecule of B_2O_3 [$=B_4O_9Na_6$] is "gewichtsbeständig."

Prof. Karl Langenbeck, of Zanesville, Ohio, kindly consented to carry out some experiments on the volatilization of borax on a larger scale in kilns, making use of pyrometers. With the approval of Prof. Langenbeck, I herewith add his interesting

[1] G. Schaffgotsch, *Pogg. Ann.*, 107, 427. Ueber die Bestimmung der Borsäure und über die Flüchtigkeit der Borsäure.

communications on the subject which are in perfect accord with the results obtained in the laboratory.

I. JANUARY 30, 1894.

12.3036 grams of borax glass were placed in a small platinum dish and set in a fire-clay capsule four inches in diameter and four inches deep, and this placed next to the pyrometers of a kiln.

From incipient redness to the melting down of Seger's pyrometric cone No. 9, took about forty-eight hours when the firing was discontinued and the kiln allowed to cool, which in about twelve hours, was no longer red.

In other words the borax glass was at a red heat about sixty hours, and reached the temperature of the melting point of Seger's pyrometric cone No. 9, (=1410° C.). On removal from the kiln the inside of the clay capsule was heavily glazed and the borax glass in the platinum dish found to weigh 6.2776 grams, hence 6.0260 grams had been volatilized, or 48.98 per cent.

II. FEBRUARY 6, 1894.

5.7698 grams $Na_2B_4O_7$ exposed to the heat of Seger's pyrometric cone No. 7 (1350° C.) lost 1.2926 grams or 22.40 per cent. This heat took ten hours less to reach and cooled about two hours more quickly, hence the specimen was about twelve hours less under a red heat.

9.2036 grams $Na_2B_4O_7$ exposed to the heat of the melting point of an alloy fifteen per cent. Ag, eighty-five per cent. Au (about 1050° C.) lost 0.7259 gram or 7.88 per cent.

To reach this heat from very low redness took about twenty hours, and the cooling to blackness six hours.

It looks very much as if it did not take so very much heat to begin the volatilization, and that the duration of fire rather than the temperature determines the amount of loss.

III. FEBRUARY 13, 1894.

7.5803 grams borax glass were exposed in a platinum dish to a heat, which was just sufficient to melt silver (954° C.) and by careful regulation of the gas this temperature was held, within very narrow limits for three hours.

The furnace is an up and down draught made by Geith, of Coburg, Germany, from designs of Seger, and has a zone of at least seventy-five cubic inches that is perfectly uniform in heat. The dish of borax glass and the pyrometric trials were placed in the center of this zone.

The dish lost in three hours 0.1115 grams or 1.47 per cent.

SUMMARY OF THE RESULTS OBTAINED BY PROF. LANGENBECK.

Amount of borax glass, grams.	Duration of heat, hours.	Maximum temperature.	Means of measuring the temperature.	Loss, grams.	Loss in per cent.
12.3036	60	1410° C.	Seger's cone, No. 9.	6.0260	48.98
5.7698	48	1350° C.	Seger's cone, No. 7.	1.2926	22.40
9.2036	26	1050° C.	Alloy 15 % Ag 85 % Au.	0.7259	7.88
7.5803	3	954° C.	Ag.	0.1115	1.47

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI. XLVI.]

ON THE VOLATILITY OF SODIUM FLUORIDE.[1]

BY SIGMUND WALDBOTT, PH.D.

THE analyses mentioned in Experiments A III and A IV of the foregoing communication did not at first give perfectly satisfactory results. In the endeavor to ascertain the cause of the deficiency, the analytical method employed was subjected to a careful examination.

This method, as described by A. Reischle,[2] is based on the principle that boric acid can be easily driven off from a borate by mixing it with six times its weight of resublimed ammonium fluoride, and heating carefully until all the boron is volatilized as ammonium borofluoride.

The residue, consisting of the fluorides of the metals that were combined with boric acid, is then treated with sulphuric acid and evaporated to dryness. The sulphates are ignited and weighed, and the amount of boric acid, if desired, is calculated from the difference between the original weight and the weight of the oxides present in the sulphates.

[1] Read before the Cincinnati Section, February 15, 1894.

[2] A. Reischle, *Ztschr. anorg. Chem.*, 4, 111-116. Abst. in *J. Chem. Soc.*, *1893*, (abstracts) p. 491.

This process, according to comparative tests made by Reischle, has proved to be the best of all known methods for determining boric acid indirectly. Several analyses carried out in the laboratory of the University of Cincinnati confirm its reliability.

Experience shows, however, that a few precautions must be closely observed in order to insure accurate results.

The ammonium fluoride employed must be resublimed, or at least the residue left on sublimation must be carefully determined and the necessary deduction made from the final weighing.

Another source of possible error seemed to lie in the volatility of the alkaline fluorides at a comparatively low temperature, and some abnormal results recorded by Reischle, were probably due to this cause.

As nothing has been published on this subject it seemed desirable to examine closely the behavior of sodium fluoride, at least at varying temperatures, and bring the results of the study to bear upon the details of the Reischle method.

The sodium fluoride employed was chemically pure and procured from C. Schuchardt in Görlitz.

The following experimental results were obtained:

I.

NaF not dried, = 0.5605 gram.
Heated over the Bunsen burner, = 0.5495 gram.
Heated again for two minutes, = 0.5490 gram.

This weight, 0.5490 gram of dry NaF, was further heated as follows:

Time of heating, minutes.	Mode of heating.	Loss each time, gram.	Total loss, gram.	Total loss in per cent.
2	Moderate blast flame	0.0040	0.0040	0.71
6	Bunsen burner with chimney, crucible slightly uncovered	0.0020	0.0060	1.09
2	Blast-flame, crucible uncovered	0.0167	0.0227	4.1
12	Bunsen burner with chimney, crucible slightly uncovered	0.0060	0.0287	5.2

II.

NaF not dried, = 0.2775 gram.
Heated over Bunsen burner to constant weight, = 0.2714 gram.

This weight, 0.2714 gram of dried NaF, was further heated as follows:

Time of heating, minutes.	Mode of heating.	Loss each time, gram.	Total loss, gram.	Loss in per cent.
6	Bunsen burner, crucible slightly uncovered	0.0039	0.0039	1.4
5	Bunsen burner, crucible slightly uncovered	0.0034	0.0073	2.7
5	Bunsen burner, lid off, contents half melted	0.0047	0.0120	4.4
10	Small flame, bottom just red hot, crucible slightly covered	0.0010	0.0130	4.9
15	Same, but flame slightly reduced	0.0003	0.0133	4.9

It follows from these experiments that the full flame of a Bunsen burner, if applied to 0.549 gram of sodium fluoride, will cause a loss of nearly 0.4 per cent. in six minutes, and if applied to 0.2714 gram will cause a loss of 1.4 per cent. in six minutes, while if the flame be reduced so that it will hardly redden the bottom of the covered platinum crucible there will be no very appreciable loss in fifteen minutes.

By observing these two precautions—subjecting sufficient material to analysis to yield not less than 0.6 gram sodium fluoride and applying as little heat as possible—the Reischle method gives excellent results, and the slight discrepancy between the results of the analysis in Experiment A V of the preceding paper, executed after the fact of the volatilization of sodium fluoride was ascertained, and the results of the analyses in experiments A III and A IV is readily accounted for.

In conclusion I wish to express to Prof. Norton my sincerest thanks for the many courtesies extended to me during these experiments. I feel likewise much indebted to Prof. Langenbeck for his kindness in having carried out the experiments on a larger scale as before recorded.

CINCINNATI, MARCH 21, 1894.

ELECTROLYTIC SEPARATIONS.

BY EDGAR F. SMITH AND HENRY E. SPENCER.

Received May 5, 1894.

I. SILVER FROM COPPER.

THE literature relating to electrolysis contains two suggestions bearing upon the separation of these metals. The first is that of Classen, (Quantitative Analyse durch Elektrolyse, dritte Auflage, p. 124). In reality this is not an electrolytic method

as the author proposes to first separate the metals by precipitating out the silver as oxalate, filtering off the same, dissolving it in potassium cyanide, and then decomposing this solution of the double cyanide of silver and potassium by means of the electric current. The double oxalate of copper and ammonium being soluble in water is filtered from off the insoluble silver oxalate, and the copper is then deposited from this solution by the current. No data obtained in the actual use of the method appear to have been published. The insolubility of silver oxalate in ammonium oxalate is not generally conceded (Rose, Analyt. Chemie, **1**, 342), so that it might well be expected, if this statement be true, that the deposit of copper would contain silver. Experiments were instituted to ascertain how accurate the method really was. The results of a few are given below. They are at the least quite instructive.

Experiment 1.—Ten cc. of a cold saturated solution of ammonium oxalate were added to a solution containing fifty cc. of copper sulphate (= 0.2284 gram of metallic copper) and ten cc. of silver nitrate (= 0.1000 gram of metallic silver). The precipitated silver oxalate was filtered and washed with ten cc. of an ammonium oxalate solution and later with pure water. The washings were colorless and the filtrate was perfectly clear, not the slightest turbidity being observed. The liquid, now 200 cc. in volume, was heated to 50° C., and electrolyzed with a current of 3-4 cc. of electrolytic gas per minute. This procedure was as nearly like that prescribed by Classen (Elektrolyse, pp. 78, 124) as it could be, since that chemist fails to give details, leaving the same to the student for adjustment. The precipitation of the copper was rapid and in every respect satisfactory. The deposit of copper weighed 0.2285 gram. Apparently the separation was complete and in no way lacking. However, upon dissolving the copper in dilute nitric acid, diluting with water and adding dilute hydrochloric acid a decided cloudiness was produced. This was found to be *due to silver chloride.*

Experiment 2.—In this trial the quantity of copper was reduced to 0.1142 gram. The silver present equaled 0.1 gram. Twenty-five cc. of ammonium oxalate were used for the precipitation and eleven more for the washing. In other respects the

conditions were similar to those in Experiment 1. The copper deposit weighed 0.1140 gram, instead of 0.1142 gram as required by theory, *yet it contained a very decided amount of silver*, which was revealed upon examining the copper.

Experiment 3.—The details here were analogous to those in Experiment 1. The precipitated copper weighed 0.2283 gram, *but after solution gave 0.0012 gram silver chloride equal to 0.0009 gram metallic silver.*

Experiment 4.—This was similar to experiment 2. The precipitate of copper weighed 0.1134 gram. It was 0.0008 gram low, but notwithstanding it showed on examination the presence of 0.0009 gram of silver.

Many more trials were made with varying amounts of copper, silver, and ammonium oxalate, but in every instance silver showed itself upon examining the precipitated copper. The inevitable conclusion is then that, however insoluble silver oxalate may be in the absence of other metals when copper is present with it, weighable amounts do pass into solution. Care was taken not to electrolyze solutions that were not absolutely clear. At times great difficulty was experienced in getting a clear filtrate from the silver oxalate. All cloudy filtrates were rejected. The results given above demonstrate that the suggestion of Classen (*loc. cit.*) with reference to the separation of silver and copper is not entitled to any consideration on the part of those who are engaged in electrolytic studies.

From an article published in the *Ztschr. angew. Chemie*, 696 (1892), by Rüdorff, it would seem that this chemist also failed, in using Classen's method, to obtain satisfactory results. The experiments in this communication are, therefore offered as a confirmation of Rüdorff's observations so far as concerns the separation of silver and copper.

The second suggestion in regard to the electrolytic separation of these two metals was offered by Smith and Frankel (*J. Frank. Inst.*, 1889; Smith's Electrochemical Analysis, p. 100). They electrolyzed a solution containing the double cyanides in the presence of an excess of alkaline cyanide. Numerous repetitions of their method, made in this laboratory, confirm their observation. Rüdorff (*loc. cit.*) also found it satisfactory. The time-

factor can, as will be noticed below, be much reduced by merely electrolyzing the solution at a temperature ranging from 65° to 70° C. The method in consequence is rendered more serviceable. Results obtained in this way follow:

Experiment 1.—A solution under electrolysis contained 0.1 gram of metallic silver and 0.1140 gram of metallic copper. The quantity of potassium cyanide present equaled 1.8 grams. The temperature of the liquid was maintained at 65° C., throughout the entire decomposition. The current was $N.D_{100}=0.07$ ampere. The total dilution of the solution equaled 200 cc. The time required for the complete precipitation of the silver was about three hours. The deposit weighed 0.0996 gram; it did not contain copper.

Experiment 2.—In this trial the conditions were similar to those in Experiment 1. The silver deposit weighed 0.1 gram. It contained no copper.

A silver dime was dissolved and the solution diluted to a definite volume. Twenty-five cc. of this solution contained 0.1081 gram of metallic silver. One gram of potassium cyanide was added to the solution and the whole then diluted to 200 cc. The temperature of the liquid during the electrolysis was 60° C. The time of precipitation occupied three hours. The silver deposit weighed 0.1080 gram; it was free from copper.

Fifty cc. of the coin solution (=0.2162 gram of metallic silver) were mixed with two grams of potassium cyanide, diluted with water to 225 cc., heated to 65° C., and electrolyzed with a current of $N.D_{100}=0.07$ ampere. The precipitated silver weighed 0.2153 gram.

The method of Smith and Frankel, as thus modified is applicable where results are desired in a comparatively short time-period.

2. MERCURY FROM COPPER.

These metals were also fully separated from each other by the electrolytic decomposition of their double cyanide solution (Smith and Frankel, *Am. Chem. J.*, **11**, 264, 104; Smith and McCauley, *J. Anal. Appl. Chem.*, **5**, 489, and *Ber. d. chem. Ges.*, **24**, 2936; also Freudenberg, *Ztschr. phys. Chem.*, **12**, 113). No difficulty attends the separation, and possibly the only objection

that could be offered to the method is, that considerable time is required for its completion. As in the case of silver and copper it is only necessary to apply a gentle heat to the solution undergoing electrolysis and the time-factor will be greatly reduced. For example:

Experiment 1.—A solution of 200 cc. volume, containing 0.2167 gram of metallic mercury, 0.2156 gram of metallic copper, and two grams of potassium cyanide was heated to 65° C. and electrolyzed with a current of $N.D_{100} = 0.08$ ampere. The precipitation was finished in three and one-half hours. The deposit of mercury was adherent and weighed 0.2168 gram. It contained no copper.

Experiment 2.—Here the conditions were nearly like those in (1). The current of $N.D_{100} = 0.06$ ampere acted for a period of four hours. The precipitated mercury weighed 0.2169 gram, but it did not contain copper.

Experiment 3.—The temperature of the solution was 70° C. The current of $N.D_{100} = 0.08$ ampere acted through four hours. The mercury weighed 0.2170 gram. It contained no copper.

Experiment 4.—In this trial the quantity of each metal was half the amount given in the preceding experiments. But one gram of potassium cyanide was present. The current of $N.D_{100} = 0.08$ ampere acted three hours upon the solution heated to 70° C. The precipitated mercury weighed 0.1083 gram. Copper was not found in it.

3. SILVER FROM CADMIUM.

These metals have usually been separated electrolytically when present in nitric acid solution. As both are precipitated by rather feeble currents form solutions containing them as double cyanides, it did not occur to the writers until recently that they could also be separated from each other in a solution of this nature. The two experiments which follow show that such is indeed the case. The separation cannot be made in a cold solution. The silver will always be contaminated with cadmium. The most favorable conditions are noted in the examples here given.

Experiment 1.—A solution of 200 cc. volume contained 0.1000 gram of metallic silver, a like quantity of metallic cadmium, and

three grams of potassium cyanide. It was heated to 65° and then electrolyzed for three and one-half hours with a current of $N.D_{100} = 0.04$ ampere. The precipitated silver weighed 0.1004 gram. No cadmium was found in it. The poles were separated two inches from each other.

Experiment 2.—Operating with conditions just like those in experiment 1, the deposit of silver weighed 0.0999 gram.

UNIVERSITY OF PENNSYLVANIA,
April 23, 1894.

THE ACTION OF PHOSPHORUS PENTACHLORIDE UPON MOLYBDENUM TRIOXIDE.

BY EDGAR F. SMITH AND GEORGE W. SARGENT.

Received May 5, 1894.

THE action of phosphorus pentachloride upon the trioxides of tungsten and of molybdenum has been the subject of investigation by Schiff,[1] Teclu,[2] and Piutti.[3] Schiff announced that with tungstic acid and the pentachloride the products were in the main phosphorus oxychloride and a brown colored tungsten oxychloride. Teclu, upon repeating Schiff's experiments, obtained phosphorus oxychloride and the *hexachloride of tungsten*. This was the result when working with one part of WO_3 and three parts of phosphorus pentachloride. The mixture was heated in sealed tubes. Piutti substituted molybdenum trioxide and hoped to get a corresponding molybdenum *hexachloride*. This he did not realize; instead, he obtained a compound which gave results on analysis that led to the formula $MoCl_5.POCl_3$. Along with the dark-green colored crystals of this compound there was a reddish-brown liquid. The tube, after being opened, and as soon as the liquid was removed, was connected with a Woulff bottle to which a drying tube was attached. The other end of the sealed tube was opened and connected with a carbon dioxide generator. The tube was next surrounded with water at 80°, and a current of carbon dioxide conducted through it, when the green colored crystals sublimed. They were carefully collected and gave the results from which was deduced the formula given above. We have repeated the experiment of Piutti under

[1] *Annalen der Chemie*, **102**, 115.
[2] *Annalen der Chemie*, **187**, 255.
[3] *G. ch. italiana*, **9**, 538.

slightly modified conditions. Thus, we exposed 1.5 grams molybdenum trioxide and ten grams of phosphorus pentachloride in a sealed tube, filled with chlorine, to a temperature of 175° C. The sides of the tube, on cooling, were covered with greenish-black crystals. One end of the tube was broken open, quickly connected with a dry flask, after which the other end was opened and attached to a delivery tube in union with a chlorine generator. As the chlorine gas was conducted through the tube a gentle heat was applied to the latter, when a colorless liquid distilled over and was carefully collected. Later the greenish-black crystals sublimed and were collected separately in a dry vessel. The analysis of the colorless liquid just mentioned indicated it to be phosphorus oxychloride. The greenish-black solid was rapidly weighed out in weighing bottles. The vessel containing the portion intended for the chlorine determination was, after weighing, uncorked under water and the substance allowed to gradually enter the water. The disengaged gases were thus wholly absorbed.

Chlorine Determinations.—(1) 0.3702 gram substance gave 1.0881 gram silver chloride, equal to 0.2720 gram chlorine, or 73.47 per cent. (2) 0.3103 gram substance gave 0.9074 gram silver chloride, equal to 0.2268 gram chlorine, or 73.14 per cent.

Phosphorus Determinations.—(1) 0.5610 gram substance gave 0.1375 gram magnesium pyrophosphate, equivalent to 6.84 per cent. phosphorus. (2) 0.7991 gram substance gave 0.1914 gram magnesium pyrophosphate, equal to 6.67 per cent. phosphorus.

Molybdenum Determination.—The substance was digested with ammonium sulphide, and from this solution hydrochloric acid precipitated the trisulphide, which was changed to disulphide and weighed as such. 0.2385 gram material gave 0.0457 gram, equal to 19.17 per cent. Mo.

From these figures we deduce an atomic ratio, which would point to our compound as being a union of one molecule of molybdenum pentachloride with one molecule of the phosphorus haloid—$MoCl_5.PCl_5$. The theoretical percentages in this case are:

Mo = 19.91 per cent., Cl = 73.65 per cent., P = 6.43 per cent.

Our compound is greenish-black in color and decomposes

quite easily. The conditions under which we operated being slightly different from those of Piutti, it is not surprising that our product should be different. We used an excess of the phosphorus haloid and took care that the tube in which the reaction occurred contained chlorine gas. Subsequently we also distilled out the phosphorus oxychloride in a current of chlorine, and did not use carbon dioxide until after the removal of the liquid, and not while the tube was exposed to a gentle heat. The reaction which occurred with us may be, perhaps, represented as follows:

$$2MoO_3 + 8PCl_5 = 6POCl_3 + 2MoCl_5.PCl_5 + Cl_2.$$

With even a larger excess of the phosphorus haloid the same product was found, so that it is hardly probable that we can hope to arrive at the hexachloride of molybdenum through this reaction.

UNIVERSITY OF PENNSYLVANIA,
April 26, 1894.

SEPARATION OF TITANIUM FROM IRON.

BY CHARLES BASKERVILLE.

Received April 16, 1894.

IN the recent literature which I have been able to consult, the separation of titanium from iron by means of sulphurous acid, has been confined to the sulphates of these two metals. This process is long and tedious and often unsatisfactory.

If a neutralized solution of titanium and iron chlorides, of not too great dilution, be boiled with an excess of sulphurous acid, the iron becomes deoxidized at once and a white flocculent precipitate of titanium settles out. By this means the titanium is obtained free from iron and requires no re-solution and second precipitation, as is frequently necessary for purification when precipitated from the sulphate. If the sulphate be changed into a chloride by precipitation with ammonium hydroxide and dissolving again in dilute hydrochloric acid and neutralizing the excess of acid with ammonium hydroxide, the separation is easily effected. The accuracy of the method is shown by the two following analyses:

	Found.	Used.
TiO_2	0.0322	0.0308
TiO_2	0.0317	0.0314

The tedious boiling with sulphurous acid is avoided. A clean precipitate, which settles well and does not cling tenaciously to the sides and bottom of the beaker, filters rapidly and easily washed with hot water, is obtained. Salts of aluminum remain in solution.

UNIVERSITY OF NORTH CAROLINA.

NEW BOOKS.

THE TANNINS. A MONOGRAPH ON THE HISTORY, PREPARATION PROPERTIES, METHODS OF ESTIMATION AND USES OF THE VEGETABLE ASTRINGENT, WITH AN INDEX TO THE LITERATURE OF THE SUBJECT. BY HENRY TRIMBLE, Ph.M. Volume 2, pp. 172. Philadelphia: J. B. Lippincott & Co. 1894. Price, $2.

The first volume of this work which appeared in 1892, was devoted to a general consideration of the subject and to gallotannic acid. The present volume deals primarily with the technically important tannins from the several species of oak bark and in a minor degree with those from mangrove, canaigre, and chestnut.

The tannins are usually dismissed by the chemist with the statement that they belong to a class of compounds about which very little is known and a few qualitative reactions at most, are given as characterizing them. Nevertheless they are of such importance that every one should know something of them. The author has endeavored to make an understanding of them possible by suggesting in some introductory remarks a method of study in which it is recommended to first investigate the sources of a tannin, then its history, method of preparation, properties, and finally a process for estimating it. It is usual for a chemist to begin with the last one of these; namely, the method of estimation and the result is invariably a failure.

With the exception of the historical chapters, this volume is made up almost entirely of the results of original research and the results of this work may best be understood by quoting from the final chapter, entitled Conclusions. "In looking over the composition of these tannins discussed in the volume, and comparing them with what appeared to be trustworthy results obtained in recent years by other investigators, we find that they

all arrange themselves according to their percentage of carbon and hydrogen into the following two groups:

	I. The gallo-tannin group.	II. The oak-tannin group.
Carbon	52.17 per cent.	60.00 per cent.
Hydrogen	3.10 " "	5.00 " " "

The tannins from nutgalls, chestnut wood and bark, pomegranate bark and sumac are classified under the first group, while those from oak bark, mangrove, canaigre, rhatany, kino, catechu, and tormentil, are found to fall within the limit of the second group.

This is nearly the old classification of "iron-blueing" and "iron-greening" tannins, but we believe with this important difference that oak-tannins so far as investigated give a green with salts of iron and not a blue as usually stated in the books. The blue color with salts of iron, the author claims, is obtained only with infusions of oak bark, and this is due to the presence of an iron-blueing coloring matter which accompanies the tannins.

S. P. S.

A System of Instruction in Qualitative Chemical Analysis. By Arthur H. Elliott, Ph.D., published by the author. N. Y. 1894. Price $2.00.

This treatise on qualitative analysis is neat in general appearance, printed in clear type and the nomenclature used is good. There is one feature of it; namely, the almost entire absence of equations representing the nature of reactions, which will bear criticism. It is impossible without a most elaborate system of experiments performed before the study of qualitative analysis is begun, to make students so familiar with the nature of chemical reactions, that these can be entirely neglected. Moreover, the average instructor of the subject prefers to keep the reactions constantly before the student as would be the case if they were introduced into the text.

It is easy to understand why such a treatise might be adopted by those engaged in the teaching of students of pharmacy and medicine, as the latter seldom enter deeply enough into the subject to consider the exact nature of the reactions involved. While leaving equations to be explained by the instructor

many minor points of manipulation are treated at unnecessary length. These might have been explained once for all beforehand.

A good feature is the mention of the occurrence in nature and in commerce of compounds of the element under discussion, a feature which is often ignored in books of its scope.

The chapters on the separations and detection of acids and bases are well written.

FRED'K W. SPANUTIUS.

"THERMODYNAMICS OF REVERSIBLE CYCLES IN GASES AND SATURATED VAPORS." BY M. I. PUPIN, PH.D.; edited by Max Osterberg. 114 pp. New York: John Wiley & Sons. 1894.

This little volume contains a "full synopsis of a ten weeks' undergraduate course of lectures," arranged (with the author's sanction) by a student of Columbia College. The course is designed as a theoretical introduction to a practical course in heat engines, not to a general course in physical chemistry. The Calculus is used throughout, but the mathematical notation is somewhat relieved by illustrations. The two laws are discussed successively with reference to perfect gases and Carnot's cycle. The integral and the differential equations of the indicator diagram are quite happily compared to Keppler's laws of planetary orbits as a whole, and Newton's successful analysis of these orbits into their minutest parts under the law of gravitation.

Steam is taken as the familiar type of saturated vapors; special emphasis is placed on the discussion of adiabatic and isothermal expansion; and reasons are given that the prevailing types of steam engines are not strictly reversible. R. B. W.

SELECT TABLES FROM THE U. S. PHARMACOPOEIA, 1890. REPRINTED FOR READY REFERENCE IN DAILY PRACTICE. Published by the Committee of Revision. Philadelphia: Agents, P. Blakiston, Son and Company. 1893.

The list comprises: Alphabetical List of Volumetric Assays; Alcoholometric Table, according to E. R. Squibb; Saturation Tables; Equivalents of Weights and Measures, customary and metric; Table of Thermometric Equivalents; List of the Prin-

cipal Pharmacopoeial Chemicals and Reagents, with their molecular weights; and Table of Atomic weights, according to L. Meyer and K. Seubert.

These respective tables are on 8vo. heavy paper for mounting on cardboard and hanging in the office or laboratory.

While the chemist may not use the whole Pharmacopoeia, these tables are just that part which will be found very useful to him. We cannot refrain from suggesting, however, that the practical chemist would make no mistake in familiarizing himself with the chemical portions of the whole book.

H. T.

NOTES.

Preparation of Standard Iodine Solutions.—The usual directions given for the preparation of standard solutions of iodine, to grind in a mortar, with a small quantity of water, the proper proportions of iodine and potassium iodide, transfer to the graduate-vessel and dilute, may be improved upon, both as to time required and danger of accidental loss of material, by the following method:

Iodine and potassium iodide, in the ratio of about two to three respectively, are carefully transferred to a graduate-flask and a weight of water added not greater than the weight of iodine used. The flask is then to be shaken until the scales of iodine disappear, care being taken not to splash the solution upon the stopper of the vessel. The required dilution is best made slowly with constant shaking. Three to five minutes are usually sufficient for the preparation of the solution and the rapidity and ease with which it may be accomplished largely depends upon using a minimum amount of water at first.

February 6, 1894. DAVID HANCOCK.

Meeting of the Association of Official Agricultural Chemists.—The Executive Committee of the Association of Official Agricultural Chemists has decided to call the Annual Meeting of the Association for August 23, 24, and 25, 1894. The meetings will

be held in the Lecture Room of the National Museum, at Washington, D. C., beginning at 10 o'clock on Thursday, August 23.

The reporters for the meeting are as follows: Phosphoric acid—B. W. Kilgore, Raleigh, N. C. Nitrogen—J. M. Bartlett, Orono, Me. Potash—H. J. Wheeler, Kingston, R. I. Soils and ash—A. M. Peter, Lexington, Ky. Dairy products—F. H. Farrington, Champaign, Ill. Foods and feeding stuffs—H. J. Patterson, College Park, Md. Fermented liquors—Geo. F. Colby, Berkeley, Cal. Sugar—G. L. Spencer, Washington, D. C.

The co-operation of European chemists has been invited in the analytical work and several acceptances of the invitation have been received. It is urged upon all members who have communications to make to the Association to bring them properly prepared and ready for printing. Much delay has arisen heretofore in securing the manuscript promptly from the reporters and others presenting papers. The speedy publication of the proceedings will be greatly facilitated by bringing everything properly prepared. H. W. WILEY, *Sec'y*.

The Assimilation of Free Nitrogen.—On page thirty of the January number of this JOURNAL I spoke of the activity of a germ which assimilated free nitrogen, attributing the discovery to Winogradsky and Warington. Mr. Warington writes me that he is not entitled to any credit for this discovery and on re-reading the original article in *The Chemical News* I find that he only called attention to its activity. The mistake arose from the intimate association in my mind of Mr. Warington's name with the researches into the nature of nitrifying organisms. I make this correction at the request of Mr. Warington. H. W. Wiley.